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(54) Title: POLYMERIZATION OF OLEFINS

(57) Abstract

Selected olefins such as ethylene and α–olefins are polymerized by nickel [II] complexes of certain monoanionic ligands. The polyolefins are useful in many applications such as molding resins, film, fibers and others. Also described are many novel nickel compounds and their precursors, as well as novel ligands.

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TITLE

POLYMERIZATION OF OLEFINS

This application claims the benefit of U.S. Provisional Application No. 60/035,190, filed January 14, 1997.

FIELD OF THE INVENTION

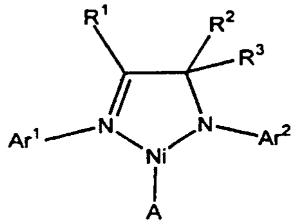
Olefins are polymerized by a catalyst system that includes a nickel[II] complexes of selected monoanionic bidentate ligands. Some of these complexes are also novel.

TECHNICAL BACKGROUND

Polymers of ethylene and other olefins are important items of commerce, and these polymers are used in a myriad of ways, from low molecular weight polyolefins being used as a lubricant and in waxes, to higher molecular weight grades being used for fiber, films, molding resins, elastomers, etc. In most cases, olefins are polymerized using a catalyst, often a transition metal compound or complex. These catalysts vary in cost per unit weight of polymer produced, the structure of the polymer produced, the possible need to remove the catalyst from the polyolefin, the toxicity of the catalyst, etc. Due to the commercial importance of polymerizing olefins, new polymerization catalysts are constantly being sought.

SUMMARY OF THE INVENTION

This invention concerns a process for the polymerization of an olefin selected from one or more of $R^{67}CH=CH_2$, cyclopentene, a styrene, a norbornene or $H_2C=CH(CH_2)_sCO_2R^{77}$, comprising, contacting, at a temperature of about -100°C to about +200°C, $R^{67}CH=CH_2$, cyclopentene, a styrene, a norbornene, or $H_2C=CH(CH_2)_sCO_2R^{77}$, optionally a Lewis acid, and a compound of the formula:



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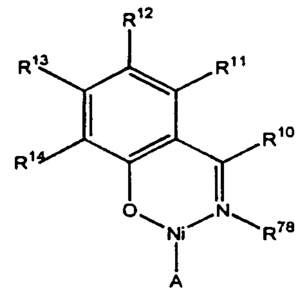

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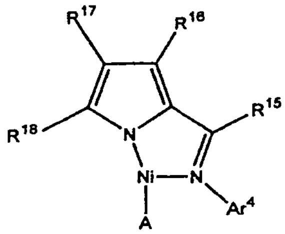

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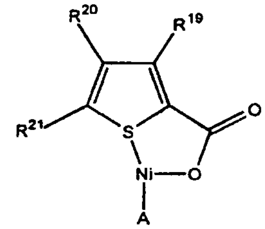

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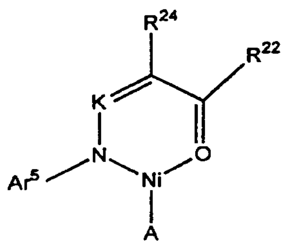

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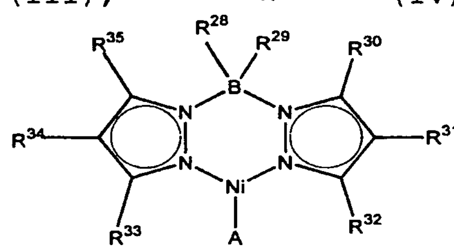

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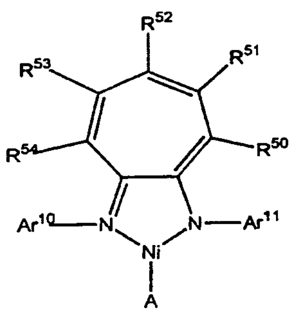

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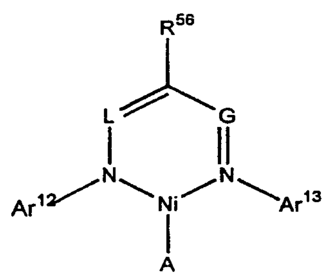

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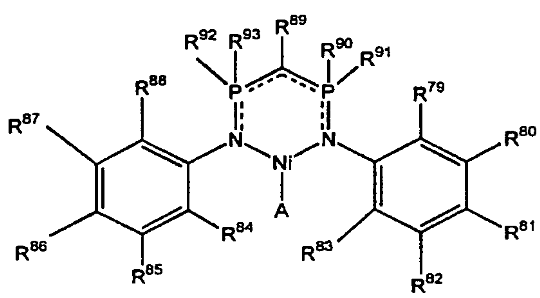

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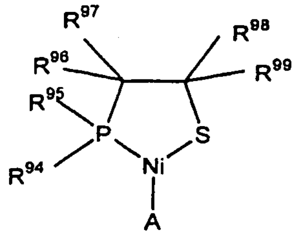

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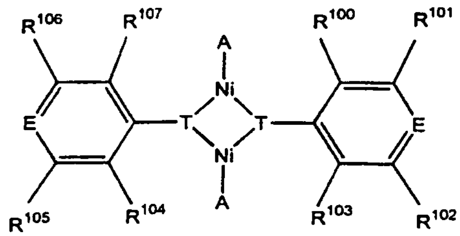

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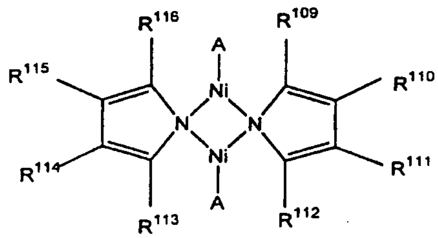


(XXXX)

wherein:

Ar^1, Ar^2, Ar^4, Ar^5, Ar^{10}, Ar^{11}, Ar^{12} and Ar^{13} are each independently aryl or substituted aryl;

R^1 and R^2 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^1 and R^2 taken together form a ring, and R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^1, R^2 and R^3 taken together form a ring;

A is a π-allyl or π-benzyl group;

R^{10} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{30}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35} R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

K is N or CR^{27};

R^{22} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{24} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{27} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{22} and R^{24} or R^{24} and R^{27} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

G and L are both N or G is CR^{57} and L is CR^{55};

R^{55}, R^{56} and R^{57} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or any two of R^{55}, R^{56} and R^{57} taken together form a ring;

R^{67} is hydrogen, alkyl or substituted alkyl;

R^{77} is hydrocarbyl or substituted hydrocarbyl;

R^{78} is hydrocarbyl or substituted hydrocarbyl;

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{94} and R^{95} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

both of T are S (sulfur) or NH (amino);

each E is N (nitrogen) or CR^{108} wherein R^{108} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

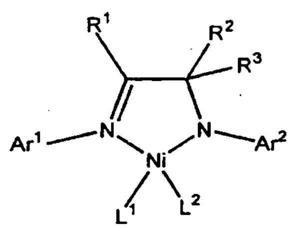
R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

s is an integer of 1 or more; and

R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that when $H_2C{=}CH(CH_2)_sCO_2R^{77}$ is present, $R^{67}CH{=}CH_2$ is also present.

This invention also concerns a process for the polymerization of an olefin selected from one or more of $R^{67}CH{=}CH_2$, a styrene, a norbornene or $H_2C{=}CH(CH_2)_sCO_2R^{77}$, comprising, contacting, at a temperature of about -100°C to about +200°C, $R^{67}CH{=}CH_2$, cyclopentene, a styrene, a norbornene, or $H_2C{=}CH(CH_2)_sCO_2R^{77}$, optionally a Lewis acid, and a compound of the formula: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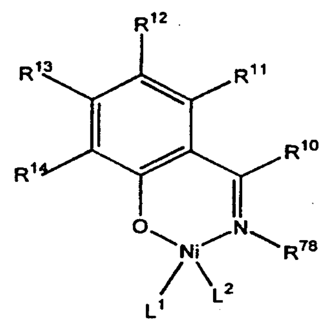
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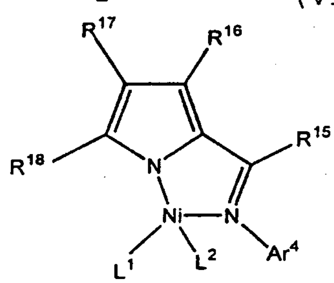
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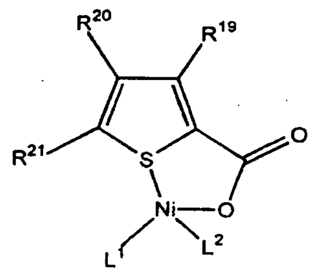
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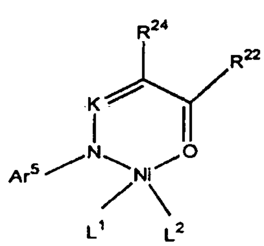
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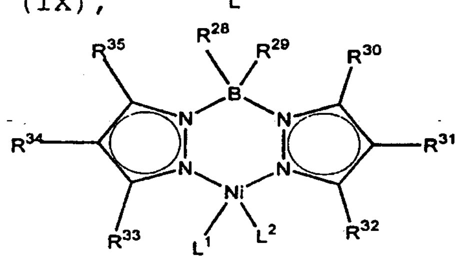
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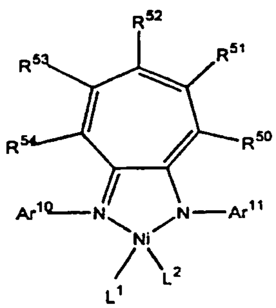

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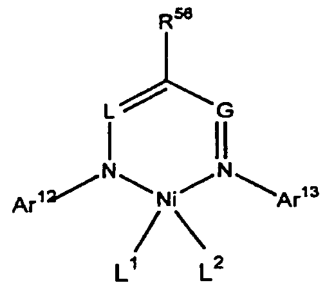

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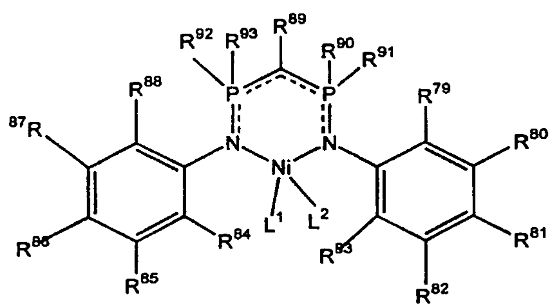

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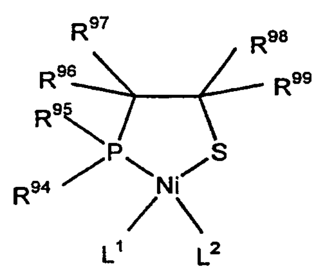

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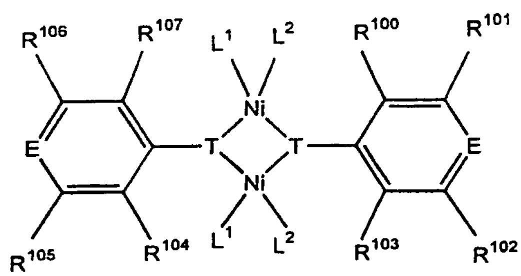

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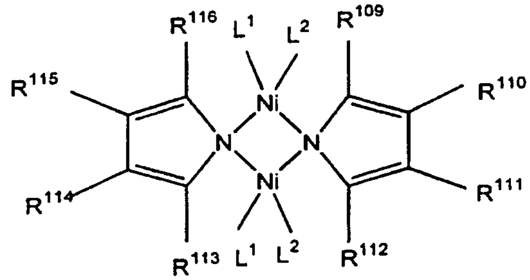


(XXXXIV),

wherein:

L^1 is a neutral monodentate ligand which may be displaced by said olefin, and L^2 is a monoanionic monodentate ligand, or L^1 and L^2 taken together are a monoanionic bidentate ligand, provided that said monoanionic monodentate ligand or said monoanionic bidentate ligand may add to said olefin;

Ar^1, Ar^2, Ar^4, Ar^5, Ar^{10}, Ar^{11}, Ar^{12} and Ar^{13} are each independently aryl or substituted aryl;

R^1 and R^2 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^1 and R^2 taken together form a ring, and R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^1, R^2 and R^3 taken together form a ring;

R^{10} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{30}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35}, R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

K is N or CR^{27};

R^{22} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{24} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{27} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{22} and R^{24} or R^{24} and R^{27} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

G and L are both N or G is CR^{57} and L is CR^{55};

R^{55}, R^{56} and R^{57} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or any two of R^{55}, R^{56} and R^{57} taken together form a ring;

R^{67} is hydrogen, alkyl or substituted alkyl;

R^{77} is hydrocarbyl or substituted hydrocarbyl;

R^{78} is hydrocarbyl or substituted hydrocarbyl;

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{94} and R^{95} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

both of T are S (sulfur) or NH (amino);

each E is N (nitrogen) or CR^{108} wherein R^{108} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

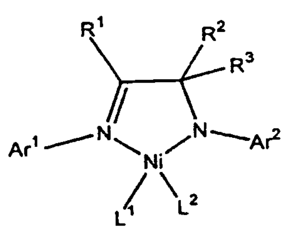
R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

s is an integer of 1 or more; and

R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that when $H_2C{=}CH(CH_2)_sCO_2R^{77}$ is present, $R^{67}CH{=}CH_2$ is also present.

Also described herein is a compound of the formula:



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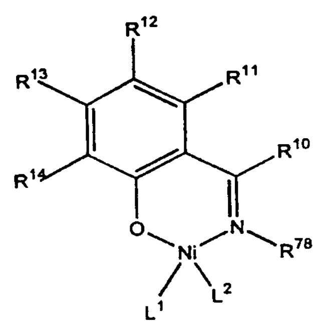

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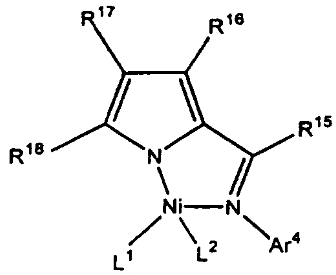

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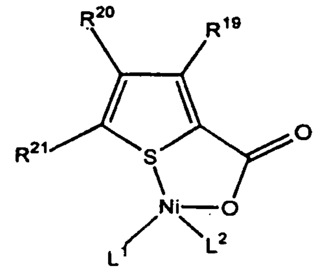

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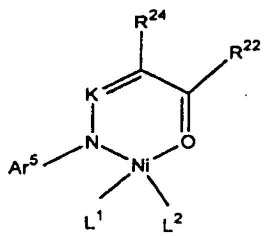

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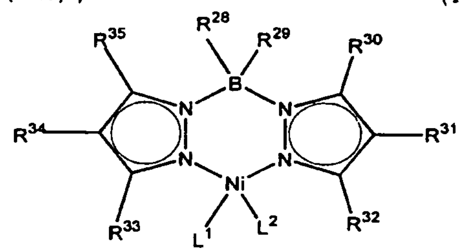

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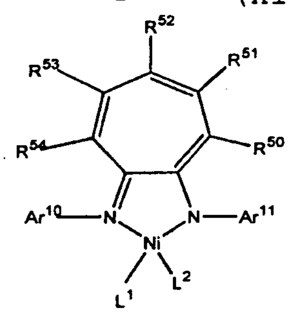

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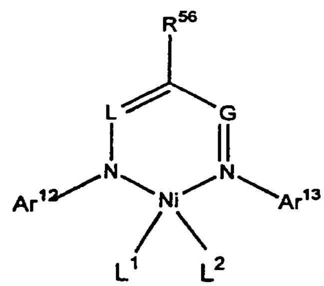

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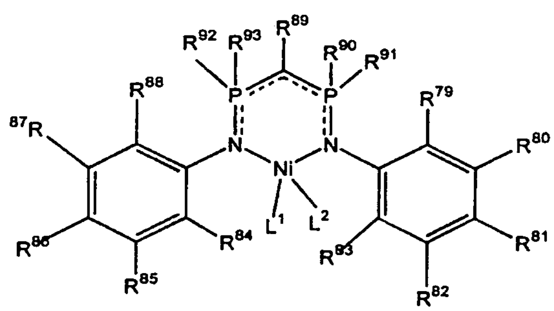

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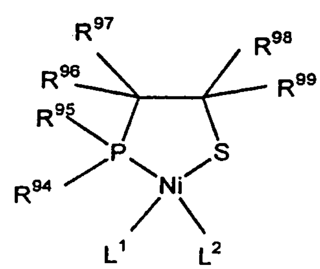

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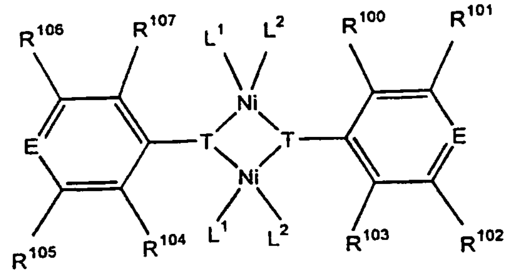

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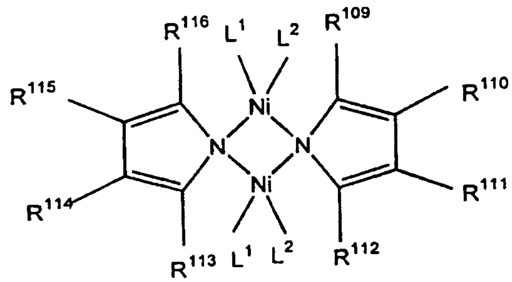


(XXXXIV),

wherein:

L^1 is a neutral monodentate ligand which may be displaced by said olefin, and L^2 is a monoanionic monodentate ligand, or L^1 and L^2 taken together are a monoanionic bidentate ligand, provided that said monoanionic monodentate ligand or said monoanionic bidentate ligand may add to said olefin;

Ar^1, Ar^2, Ar^4, Ar^5, Ar^{10}, Ar^{11}, Ar^{12} and Ar^{13} are each independently aryl or substituted aryl;

R^1 and R^2 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^1 and R^2 taken together form a ring, and R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^1, R^2 and R^3 taken together form a ring;

R^{10} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{30}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35}, R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

K is N or CR^{27};

R^{22} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{24} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{27} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{22} and R^{24} or R^{24} and R^{27} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

G and L are both N or G is CR^{57} and L is CR^{55};

R^{55}, R^{56} and R^{57} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or any two of R^{55}, R^{56} and R^{57} taken together form a ring;

R^{78} is hydrocarbyl or substituted hydrocarbyl;

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{94} and R^{95} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

both of T are S (sulfur) or NH (amino);

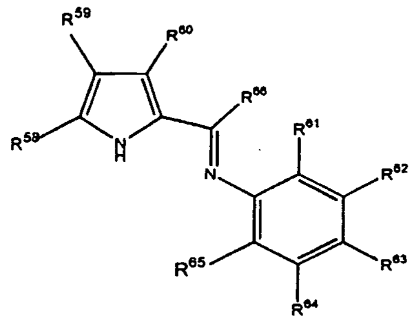
each E is N (nitrogen) or CR^{108} wherein R^{108} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group; and

R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl.

Also disclosed herein is a compound of the formula



(XXXIII),

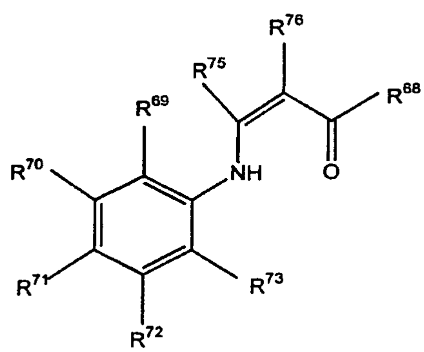
wherein:

R^{58}, R^{59}, R^{60}, R^{62}, R^{63} and R^{64} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group, and provided that any two of these groups vicinal to one another taken together may form a ring, or if vicinal to R^{61} or R^{65} form a ring with them;

R^{66} is hydrogen, hydrocarbyl or substituted hydrocarbyl; and

R^{61} and R^{65} are each independently hydrocarbyl containing 2 or more carbon atoms, or substituted hydrocarbyl containing 2 or more carbon atoms, and provided that R^{61} and R^{65} may form a ring with any group vicinal to it.

This invention also concerns a compound of the formula



(XXXVI),

wherein:

R^{68} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{76} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{75} is hydrocarbyl or substituted hydrocarbyl, and provided

that R^{68} and R^{76} or R^{75} and R^{76} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{70}, R^{71} and R^{72} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{69} and R^{73} are hydrocarbyl containing 3 or more carbon atoms, substituted hydrocarbyl containing 3 or more carbon atoms or a functional group;

and provided that any two of R^{70}, R^{71}, R^{72}, R^{69} and R^{73} vicinal to one another together may form a ring.

DETAILS OF THE INVENTION

Herein, certain terms are used. Some of them are:

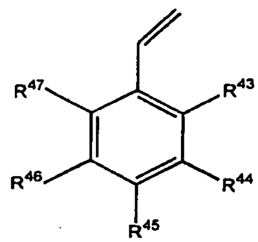
- A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein preferably contain 1 to about 30 carbon atoms.
- By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain preferably 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.
- By "(inert) functional group" herein is meant a group other than hydrocarbyl or substituted hydrocarbyl which is inert under the process conditions to which the compound containing the group is subjected. The functional groups also do not substantially interfere with any process described herein that the compound in which they are present may take part in. Examples of functional groups include

halo (fluoro, chloro, bromo and iodo), ether such as $-OR^{25}$, $-CO_2R^{25}$, $-NO_2$, and $-NR^{25}_2$, wherein R^{25} is hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near a nickel atom the functional group should not coordinate to the metal atom more strongly than the groups in compounds which are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

- By a "polymerization process" herein (and the polymers made therein) is meant a process which produces a polymer with a degree of polymerization (DP) of about 5 or more, preferably about 10 or more, more preferably about 40 or more [except where otherwise noted, as in P in compound (XVII)]. By "DP" is meant the average number of repeat (monomer) units in the polymer.
- By "aryl" herein is meant a monovalent radical whose free valence is to a carbon atom of an aromatic ring. Unless otherwise noted herein, preferred aryl groups contain carbocyclic rings, but heterocyclic rings are also included within the definition of "aryl". The aryl radical may contain one ring or may contain 2 or more fused rings, such as 9-anthracenyl or 1-naphthyl. Unless otherwise stated aryl groups preferably contain 5 to 30 carbon atoms.
- By "substituted aryl" herein is meant an aryl radical substituted with one or more groups that do not interfere with the synthesis of the compound or the resulting polymerization. Suitable substituents include alkyl, aryl such as phenyl, halo, alkoxy, ester, dialkylamino and nitro. Unless otherwise stated, substituted aryl groups contain 5 to about 30 carbon atoms.
- By a "monoanionic ligand" is meant a ligand with one negative charge.
- By a "neutral ligand" is meant a ligand that is not charged.

- "Alkyl group" and "substituted alkyl group" have their usual meaning (see above for substituted under substituted hydrocarbyl). Unless otherwise stated, alkyl groups and substituted alkyl groups preferably have 1 to about 30 carbon atoms.

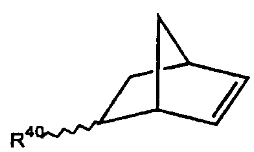
- By a styrene herein is meant a compound of the formula



(XXXIV)

wherein R^{43}, R^{44}, R^{45}, R^{46} and R^{47} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, all of which are inert in the polymerization process. It is preferred that all of R^{43}, R^{44}, R^{45}, R^{46} and R^{47} are hydrogen. Styrene (itself) is a preferred styrene.

- By a norbornene is meant ethylidene norbornene, dicyclopentadiene, or a compound of the formula

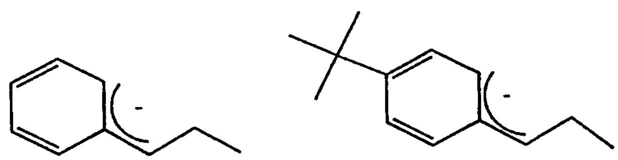


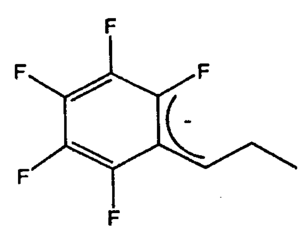
(XXXV);

wherein R^{40} is hydrogen or hydrocarbyl containing 1 to 20 carbon atoms. It is preferred that R^{40} is hydrogen or alkyl, more preferably hydrogen or n-alkyl, and especially preferably hydrogen. The norbornene may be substituted by one or more hydrocarbyl, substituted hydrocarbyl or functional groups in the R^{40} or other positions, with the exception of the vinylic hydrogens, which remain. Norbornene (itself), dimethyl endo-norbornene-2,3-dicarboxylate, t-butyl 5-norbornene-2-carobxylate are preferred norbornenes and norbornene (itself) is especially preferred.

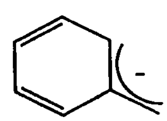
- By a π-allyl group is meant a monoanionic ligand with 3 adjacent sp^2 carbon atoms bound to a metal center in an η^3 fashion. The three sp^2 carbon atoms may be substituted with other hydrocarbyl groups or functional groups. Typical π-allyl groups include

wherein R is hydrocarbyl. By a π-benzyl group is meant π-allyl ligand in which two of the sp^2 carbon atoms are part of an aromatic ring. Typical π-benzyl groups include





and



π-Benzyl compounds usually initiate polymerization of the olefins fairly readily even at room temperature, but π-allyl compounds may not necessarily do so. Initiation of π-allyl compounds can be improved by using one or more of the following methods:

- Using a higher temperature such as about 80°C.

- Decreasing the bulk of the monoanionic ligand, such as aryl being 2,6-dimethylphenyl instead of 2,6-diisopropylphenyl.

- Making the π-allyl ligand more bulky, such as using

rather than the simple π-allyl group itself.

- Having a Lewis acid or a material that acts as a Lewis acid present while using a π-allyl or π-benzyl group, especially a functional π-allyl or π-benzyl group. Relatively weak Lewis acids such as triphenylborane, tris(pentafluorophenyl)borane, tris(3,5-trifluoromethylphenyl)borane, and poly(methylaluminoxane) are preferred. Suitable functional groups include chloro and ester.

Lewis acids may also be optionally present when compounds containing L^1 and/or L^2 are present in the polymerization, even when L^2 is not a π-allyl or π-benzyl group. It is believed that the Lewis acid, if present, may help to remove L^1 (if present) from the nickel atom, thereby facilitating the coordination of the olefin to the Ni atom. If a compound containing L^1 and/or L^2 does not act as a polymerization catalyst, it is suggested that a Lewis acid, such as those mentioned above be added to the process to determine if polymerization will then take place. Such testing requires minimal experimentation, and is illustrated in the Examples. Not surprisingly, with any particular set of polymerization process ingredients, some Lewis acids may be more effective than others.

In preferred olefins herein, R^{67} is hydrogen or n-alkyl containing 1 to 20 carbon atoms (an α-olefin), more preferably n-alkyl containing 1 to 8 carbon atoms, or more preferably hydrogen (e.g., ethylene) or methyl (e.g., propylene), and especially preferably hydrogen. A combination of ethylene and $H_2C{=}CHR^{67}$ wherein R^{67} n-alkyl containing 1 to 8 carbon atoms is also

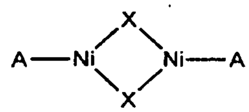
preferred, and a combination of ethylene and propylene is more preferred. It is also preferred that s is 2 or more, and/or R^{77} is alkyl, especially preferably methyl or ethyl. When $H_2C{=}CH(CH_2)_sCO_2R^{77}$ is present as one of the olefins, it is preferred that R^{67} is hydrogen.

While not all homopolymers and copolymers of the olefinic monomers useful herein can be made using the polymerization processes described herein, most homopolymers and many copolymers can be made. The following homopolymers can be readily made in these polymerization processes: polyethylene, polystyrene, a polynorbornene, poly-α-olefins (often lower molecular weight polymers obtained), polycyclopentene (often lower molecular weight polymers obtained). Attempted homopolymerization of functionalized norbornenes often does not proceed, nor do homopolymerizations of compounds of the formula $H_2C{=}CH(CH_2)_sCO_2R^{77}$. Many copolymers can be made, including ethylene/α-olefins, styrene/norbornene copolymers, copolymers of 2 or more norbornenes including functionalized norbornenes, copolymers of ethylene and cyclopentene, copolymers of ethylene and a norbornene, and copolymers of ethylene and $H_2C{=}CH(CH_2)_sCO_2R^{77}$.

Not every variation of every nickel complex listed in the various polymerizations will make every one of the polymers listed immediately above. However, many of them will make most if not all of these types of polymers. While no hard and fast rules can be given, it is believed that for polymerizations which include ethylene and/or α-olefins, steric hindrance about the nickel atom caused by substituent groups is desirable for making polymers, especially higher molecular weight polymers, while for polymers containing one or more of a styrene and/or a norbornene such steric hindrance is not as important.

The Ni[II] complexes that are useful herein for the polymerization of ethylene contain a bidentate monoanionic ligand (other than a combined L^1 and L^2)in

which the coordinating atoms are 2 nitrogen atoms, a nitrogen atom and an oxygen atom, a phosphorous atom and a sulfur atom, or an oxygen atom and a sulfur atom. Compounds of formulas (I) through (VI), (XVIII), (XXVII), and (XXXVII)-(XXXX) can be made by reaction of 2 moles of the anionic form of the ligand with one mole of the appropriate nickel allyl or benzyl precursor (XXI),


(XXI),

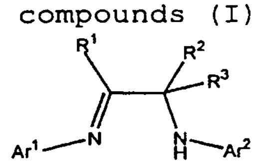
wherein X is preferably chlorine or bromine and A is a π-allyl or π-benzyl group, to form the nickel compound (see Examples 17-40 and 469-498).

Compounds of formulas (VII) through (XII), (XIX), (XXVIII), and (XXXXI)-(XXXXIV) can be synthesized by protonation of a suitable Ni[0] or Ni[II] precursor by the neutral ligand or by reaction of a suitable Ni[II] precursor with the anionic form of the ligand. Examples of suitable Ni[0] and Ni[II] precursors include Ni(1,4-cyclooctadiene)$_2$, (N,N,N′N′-tetramethylethylenediamine)NiMe$_2$, 2,2′-bipyridineNiMe$_2$, (MePPh$_2$)$_3$NiMe$_2$, [Ni(OMe)Me(PPh$_3$)]$_2$, [Ni(OMe)Me(PMe$_3$)]$_2$, NiBr$_2$, N,N,N′N′-tetramethylethylenediamine)Ni (acetylacetonate)$_2$, (1,2-dimethoxyethane)NiBr$_2$, N,N,N′N′-tetramethylethylenediamine)Ni(CH$_2$=CHCO$_2$CH$_3$)$_2$, (pyridine)$_2$Ni(CH$_2$=CHCO$_2$CH$_3$)$_2$, and (acetylacetonate)Ni(Et)(PPh$_3$). The addition of phosphine or ligand "sponges" such as CuCl, BPh$_3$ or tris(pentafluorophenyl)borane may aid such reactions.

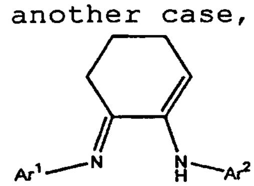
Some of the nickel compounds herein such as (XXXIX), (XXXX), (XXXXIII) and (XXXXIV) may exist as "dimers" or monomers, or in equilibrium between the two. The dimer contains two nickel atoms, each nickel atom being coordinated to L^1 and L^2, wherein L^1 and L^2 combined may be a bidentate monoanionic ligand such as a π-allyl or π-benzyl group, and both Ni atoms "share" coordination to each of the other ligands present. As

described herein, depiction of the monomeric compound also includes the dimeric compound, and vice versa. Whether any particular nickel compound is (predominantly) a monomer or dimer, or both states are detectable will depend on the ligands present. For instance it is believed that as the ligands become more bulky, especially about the nickel atom, the tendency is to form a monomeric compound.

Ligands for compounds (I) and (VII) of the formula

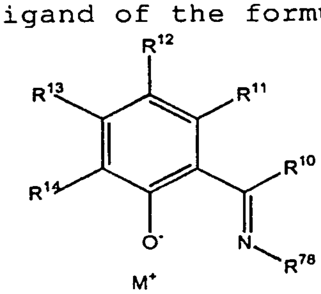

(XXII),

can be made by reaction of an alpha-diimine of the formula $Ar^1N=CR^1-CR^2=NAr^2$ with one equivalent of a compound of the formula R^3Li, see for instance M. G. Gardner, et al., Inorg. Chem., vol. 34 p. 4206-4212 (1995). In another case, a ligand of the formula


(XXIII),

can be made by the condensation of 1,2-cyclohexadione with the corresponding aromatic amine(s), see for instance R. van Asselt, et. al, Recl. Trav. Chim. Pays-Bas, vol. 113, p. 88-98 (1994). Note that in (XXIII) R^1, R^2 and R^3 taken together form a ring, with R^2 and R^3 both "part of" a double bond to the same carbon atom. These ligands can then be converted to their corresponding nickel complexes by the methods described above.

Compounds of the formula (II) can be made by the reaction of a ligand of the formula

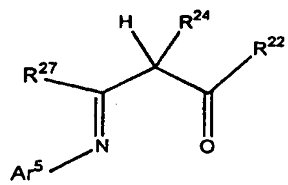

(XIII),

while compounds of the formula (VIII) can be made from the protonated form of (XIII). (XIII) can be made from the corresponding salicylaldehyde (when R^{10} is hydrogen) and aromatic amine, followed by reaction with an alkali metal base (such as an alkali metal hydride) to form the aryloxide.

(III) and (IX) can be made by reacting pyrrole-2-carboxyaldehyde with the appropriate aromatic amine to form the pyrrole-2-imine, followed by reaction with a strong base to form the pyrrole anion, and then reaction with the nickel precursors described above to form the nickel[II] complex.

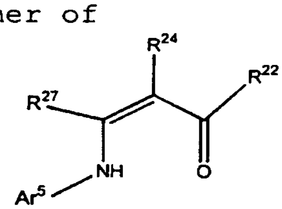
Similarly, (IV) and (X) can be formed from an alkali metal thiophene-2-carboxylate and the nickel precursors described above.

When K is CR^{27} the ligand for (V) and (XI) can be made by the reaction of the corresponding ketone (which may contain other functional groups) with an aromatic amine to give



(XXIV),

which is a tautomer of



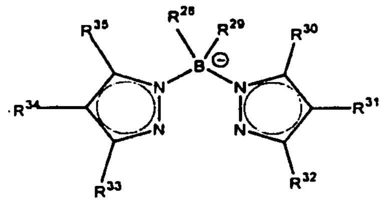
(XXV).

Useful ketones for making (V) and (XI) include ethyl acetoacetate, ethyl 2-ethylacetoacetate, isobutyl acetoacetate, t-butyl acetoacetate, S-t-butyl acetoacetate, allyl acetoacetate, ethyl 2-methylacetoacetate, methyl 2-chloroacetoacetate, ethyl 2-chloroacetoacetate, methyl 4-chloroacetoacetate, ethyl 4-chloroacetoacetate, ethyl 4,4,4-trifluoroacetoacetate, S-methyl 4,4,4-trifluoro-3-oxothiobutyrate, 2-methoxyethyl

acetoacetate, methyl 4-methoxyacetoacetate, methyl propionylacetate, ethyl propionyl acetate, ethyl isobutyrylacetate, methyl 4,4-dimethyl-3-oxopentanoate, ethyl bytyrylacetate, ethyl 2,4-dioxovalerate, methyl 3-oxo-6-octenoate, dimethyl 1,3-acetonedicarboxylate, diethyl 1,3-acetonedicarboxylate, di-t-butyl 1,3-acetonedicarboxylate, dimethyl 3-oxoadipate, diethyl 3-oxopimelate, dimethyl acetylsuccinate, diethyl acetylsuccinate, diethyl 2-acetylglutarate, methyl 2-cyclopentatecarboxylate, ethyl 2-cyclopentanecarboxylate, ethyl 4-methyl-2-cyclohexanone-1-carboxylate, ethyl 4-methyl-2-cyclohexanone-1-carboxylate, ethyl 3-(1-adamantyl)-3-oxopropionate, methyl 2-oxo-1-cycloheptanecarboxylate, N-t-butylacetoamide, 2-chloro-N,N-dimethylacetoacetamide, 4,4,4-trifluoro-1-phenyl-1,3-butanedione, 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione, 2-acetyl-1-tetralone, ethyl 2-benzylacetoacetonate, methyl 1-benzyl-4-oxo-3-piperidinecarboxylate hydrochloride, benzyl acetoacetate, acetoacetanilide, o-acetoacetotoluide, N-(2,4-dimethylphenyl)-3-oxobutyramide, o-acetoacetanisidide, 4'-chloroacetoacetanilide, and 1,1,1-trifluoro-3-thianoylacetone.

When K is N in (V) and (XI), and R^{24} is nitrile, the ligand can made by the reaction of $R^{22}C(O)CH_2CN$ with the diazonium salt of the corresponding arylamine, see for instance V.P. Kurbatov, et al., Russian Journal of Inorganic Chemistry, vol. 42, p. 898-902(1997). This paper also reviews methods of making ligands wherein K is CR^{27}.

The boron containing ligands needed for compounds (VI) and (XII),

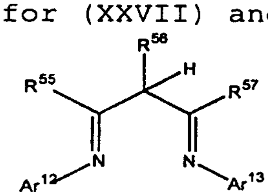


(XXVI),

can be made by known procedures, see for instance S. Trofimenko, Prog. Inorg. Chem., vol. 34, p. 115-210 (1986) and S. Trofimenko, Chem. Rev., vol. 93, p. 943-980 (1993).

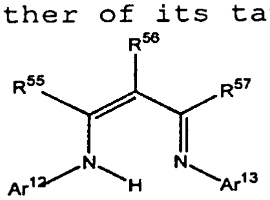
The synthesis of the tropolone-type ligands required for (XVIII) and (XIX) are described in J. J. Drysdale, et al., J. Am. Chem. Soc., vol. 80, p. 3672-3675 (1958); W. R. Brasen, et al., vol. 83, p. 3125-3138 (1961); and G. M. Villacorta, et al., J. Am. Chem. Soc., vol. 110, p. 3175-3182 (1988). These can be reacted as described above to form the corresponding nickel complex.

The ligand for (XXVII) and (XXVIII),

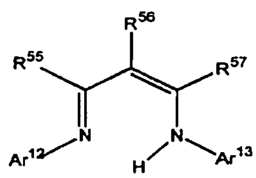


(XXIX),

or either of its tautomers,



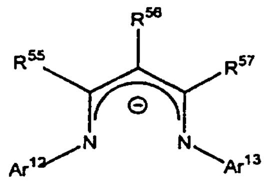
(XXX) and



(XXXI)

can be made by reaction of the appropriate α,χ-dioxo compound such as a 1,3-dione or 1,3-dial or similar compound with the appropriate aromatic amine, see for instance J. E. Parks, et al., Inorg. Chem., vol. 7, p. 1408 (1968); R. H. Holm, Prog. Inorg. Chem., vol. 14, p. 241 (1971); and P. C. Healy, et al., Aust. J. Chem., vol. 32, p. 727 (1979).

If the ligand precursor may form a tautomer, the ligand itself may usually be considered a tautomer. For instance, the monoanionic ligand derived from (XXIX) and it tautomers may be written as

 (XXXII).

In (XXVII) and (XXVIII) when L and/or G is N, the ligand can be made by the method described in Y.A. Ibrahim, et al., Tetrahedron, vol. 50, p. 11489-11498(1994) and references described therein.

The ligands for (XXXVII) and (XXXXI) can be made by methods described in Phosphorous, Sulfur and Silicon, vol. 47, p. 401 et seq. (1990), and analogous reactions.

The ligands for (XXXVIII) and (XXXXII) can be made by reacting R_2PLi (from R_2PH and n-BuLi) with propylene sulfide to form $R_2CH_2CH(CH_3)SLi$, and analogous reactions.

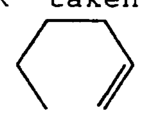
The ligands for (XXXIX) and (XXXXIII), and for (XXXX) and (XXXXIV) are commercially available. Those used herein were bought from Aldrich Chemical Co., Inc., Milwaukee, WI, U.S.A.

In the compounds (and ligands in those compounds) (I) through (XII), (XVIII), (XIX), (XXVII), (XXVIII), and (XXXVII)-(XXXXIV), certain groups are preferred. When present, they are:

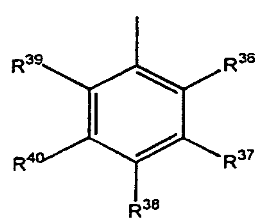
R^1 and R^2 are both hydrogen; and/or

R^3 is alkyl or aryl containing 1 to 20 carbon atoms, more preferably R^3 is t-butyl; and/or

R^1, R^2 and R^3 taken together are

 ; and/or

Ar^1, Ar^2, Ar^3, Ar^4, Ar^5, Ar^{10} and Ar^{11} are each independently

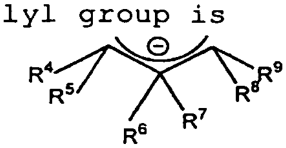
 (XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring (for example the group 9-anthracenyl), and it is especially preferred that R^{36} and R^{39} are halo, phenyl or alkyl containing 1 to 6 carbon atoms, and it is more preferred that R^{36} and R^{3} are methyl, bromo, chloro, t-butyl, hydrogen, or isopropyl; and/or

R^{78} is Ar^3, which is aryl or substituted aryl;

Ar^1, Ar^2, Ar^3, Ar^4, Ar^5, Ar^{10} and Ar^{11} are each independently 2-pyridyl or substituted 2-pyridyl;

if a π-allyl group is



(XX)

then R^4, R^5, R^6, and R^8 are hydrogen; and/or

R^4, R^5, R^6, R^7, R^8 and R^9 are hydrogen; and/or

R^4, R^5, R^6, and R^7 are hydrogen and R^8 and R^9 are methyl;

one of R^7 or R^9 is $-CO_2R^{41}$ or chloro, and the other is hydrogen, and wherein R^{41} is hydrocarbyl, preferably alkyl containing 1 to 6 carbon atoms; and/or

R^{11}, R^{12}, R^{13} and R^{14} are each independently chloro, bromo, iodo, alkyl, alkoxy, hydrogen or nitro; and/or

R^{11} and R^{12} taken together form an aromatic carbocyclic 6-membered ring; and/or

R^{14} and R^{12} are both chloro, bromo, iodo, t-butyl or nitro; and/or

R^{11} and R^{13} are methoxy;

R^{14} is hydrogen and R^{12} is nitro; and/or

one or more of R^{11}, R^{12}, R^{13} and R^{14} are hydrogen; and/or

R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, and R^{21} are hydrogen; and/or

R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} are hydrogen and R^{21} is methyl; and/or

K is CR^{27}; and/or

R^{27} is hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group; and/or

R^{27} is alkyl, more preferably methyl; and/or

R^{24} is hydrogen, alkyl, cyano, or halo, more preferably hydrogen; and/or

R^{22} is hydrocarbyl or $-OR^{117}$, wherein R^{117} is hydrocarbyl, more preferably alkyl containing 1 to 6 carbon atoms, or R^{22} is phenyl; and/or

R^{32} and R^{33} are both alkyl containing 1 to 6 carbon atoms or phenyl, more preferably isopropyl; and/or

R^{28} and R^{29} are both hydrogen or phenyl; and/or

R^{30}, R^{31}, R^{34} and R^{35} are all hydrogen; and/or

R^{31} and R^{32} taken together and R^{33} and R^{34} taken together are both a 6-membered aromatic carbocyclic ring having a t-butyl group vicinal to the R^{32} and R^{33} positions; and/or

R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are hydrogen; and/or

L is CR^{55} wherein R^{55} is hydrocarbyl, hydrogen, or substituted hydrocarbyl; and/or

G is CR^{57} wherein R^{57} is hydrocarbyl, hydrogen or substituted hydrocarbyl; and/or

more preferably R^{55} and R^{57} are both alkyl or fluorinated alkyl, more preferably methyl; and/or

R^{56} is hydrogen; and/or

Ar^{12} and Ar^{13} are both 2,6-diisopropylphenyl; and/or

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen or alkyl; and/or

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl, more preferably aryl, and especially preferably phenyl; and/or

R^{94} and R^{95} are each independently hydrocarbyl; and/or

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen or hydrocarbyl; and/or

E is N or CR^{108}; and/or

R^{108} is hydrogen or hydrocarbyl; and/or

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} is each independently hydrogen, hydrocarbyl,or halo; and/or

R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen or hydrocarbyl.

Specific preferred compounds (I)-(IV) and (VI) are given in Table A. The same groupings shown in the Table are preferred for the analogous compounds (VII)-(X) and (XII). In all of these compounds, where applicable, R^4, R^5, R^6, R^8, R^9 [in (XX) above], R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{30}, and R^{35} are all hydrogen (with the exceptions in the footnotes), R^{10} is hydrogen or methyl, R^{21} is hydrogen or methyl, and R^7 is $-CO_2CH_3$ (with the exceptions in the footnotes). In compounds wherein L_1 and L_2 appear, and especially in compounds of formula (VIII) it is preferred that L_1 is a nitrile, such as benzonitrile, p-methylbenzonitrile methyl nitrile, or pyridine or a substituted pyridine such as 2,6-dimethyl pyridine. A preferred L_2 is an alkyl group, especially methyl. L_1 and L_2 taken together may be a π-allyl or π-benzyl group, but for all compounds in which L_1 and L_2 are present (i.e. combined) it is preferred that they are not a π-allyl or π-benzyl group.

Table B give specific preferred compounds for (V), (XXXVII) and (XXXIX) as well as the corresponding compounds (XI), (XXXXI) and (XXXXIII) respectively. In all of these compounds Ar^5 is 2,6-diisopropylphenyl, K is CCH_3, R^{24}, R^{79}, R^{80}, R^{82}, R^{85}, R^{87}, R^{88}, and R^{89} are hydrogen, R^{90}, R^{91}, R^{92}, and R^{93} are phenyl.

In a specific preferred compounds (XXVII) and the corresponding (XXVIII), Ar^{12} and Ar^{13} are 2,6-diisopropylphenyl, L and G are CCH_3, and R^{56} is hydrogen.

In a specific preferred compound (XXXVIII) and the corresponding (XXXXVII), R^{94} and R^{95} are each cyclohexyl, R^{96}, R^{97} and R^{98} are hydrogen, and R^{99} is methyl.

In a specific preferred compound (XXXX) and the corresponding (XXXXIV), R^{110}, R^{111}, R^{114} and R^{115} are hydrogen and R^{109}, R^{112}, R^{113} and R^{116} are methyl.

Table A

Cmpd[c]	R^1	R^2	R^3	Ar^1 and Ar^2	Ar^3	R^{11}	R^{12}	R^{13}	R^{14}	Ar^4	R^{28}	R^{29}	R^{30}	R^{31}	R^{32}	R^{33}	R^{34}	R^{35}
Ia	a	a	a	2,6-i-Pr-Ph	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ib	H	H	t-butyl	2,6-i-Pr-Ph	-	-	-	-	-	-	-	-	-	-	-	-	-	-
IIa	-	-	-	-	2,6-i-Pr-Ph	H	t-butyl	H	t-butyl	-	-	-	-	-	-	-	-	-
IIb	-	-	-	-	2,6-i-Pr-Ph	b	b	H	H	-	-	-	-	-	-	-	-	-
IIc	-	-	-	-	2,6-Me-Ph	b	b	H	H	-	-	-	-	-	-	-	-	-
IId	-	-	-	-	2,6-Me-Ph	H	Cl	H	Cl	-	-	-	-	-	-	-	-	-
IIe	-	-	-	-	2,6-i-Pr-Ph	H	Cl	H	Cl	-	-	-	-	-	-	-	-	-
IIf	-	-	-	-	2,6-i-Pr-Ph	H	NO_2	H	NO_2	-	-	-	-	-	-	-	-	-
IIg	-	-	-	-	2,4,6-t-butyl-Ph	H	NO_2	H	NO_2	-	-	-	-	-	-	-	-	-
IIh	-	-	-	-	2,6-Br-4-Me-Ph	H	NO_2	H	NO_2	-	-	-	-	-	-	-	-	-
IIi	-	-	-	-	2,6-Me-Ph	H	NO_2	H	NO_2	-	-	-	-	-	-	-	-	-
IIj	-	-	-	-	2,6-i-Pr-Ph	H	NO_2	H	H									
IIk	-	-	-	-	2-t-Bu-Ph	H	NO2	H	NO2									
IIl	-	-	-	-	2,6-Me-Ph	H	t-butyl	H	t-butyl									
IIm	-	-	-	-	2,6-Br-4-F-Ph	H	t-butyl	H	t-butyl									
IIn	-	-	-	-	2-Cl-6-Me-Ph	H	NO2	H	NO2									
IIo	-	-	-	-	f	H	NO2	H	NO2									
IIp	-	-	-	-	2,6-i-Pr-Ph	H	I	H	I									
IIq	-	-	-	-	2,6-i-Pr-Ph	OMe	H	OMe	H									
IIr	-	-	-	-	2,6-Br-4-F-Ph	b	b	H	H									

IIs	-	-	-	-	3-Me-1-pyridyl	b	b	H	H									
IIt	-	-	-	-	2-t-Bu-Ph	b	b	H	H									
IIu	-	-	-	-	e	H	H	H	H									
IIIa	-	-	-	-	-	-	-	-	-	2,6-i-Pr-Ph	-	-	-	-	-	-	-	-
VIa	-	-	-	-	-	-	-	-	-	-	H	H	H	d	d	d	d	H
VIb	-	-	-	-	-	-	-	-	-	-	Ph	Ph	H	H	i-propyl	i-propyl	H	H

[a] R^1, R^2 and R^3 taken together are $=CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ wherein a vinylic carbon is vicinal to the amino nitrogen atom.

[b] R^{11} and R^{12} taken together form a 6 membered aromatic ring (the two fused rings together form a naphthalene group).

[c] R^7 in (XX) is $-CO_2CH_3$. All other groups in (XX) are H.

[d] R^{31} and R^{32}, and R^{33} and R^{34}, each pair taken together form a 6-membered aromatic carbocyclic ring substituted with a t-butyl group at the carbon atoms vicinal to the R^{32} and R^{33} positions.

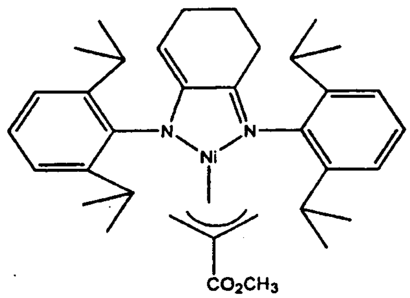
[e] R^{10} and R^{78} taken together are, respectively, $-OCH_2C(CH_3)_2-$ wherein the oxygen atom is attached to a carbon atom.

[f] 1,2,3,4-tetrahydro-1-naphthyl

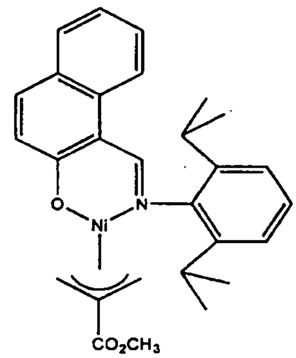
Table B

Cmpd	R^{22}	R^{81}	R^{83}	R^{84}	R^{86}	T	E	R^{100}	R^{101}	R^{102}	R^{103}	R^{104}	R^{105}	R^{106}	R^{107}
Va	OMe	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Vb	Me	-	-	-	-	-	-	-	-	-	-	-	-	-	-
XXXVIIa	-	Me	H	H	Me	-	-	-	-	-	-	-	-	-	-
XXXVIIb	-	H	Me	Me	H	-	-	-	-	-	-	-	-	-	-
XXXIXa	-	-	-	-	-	S	N	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl
XXXIXb	-	-	-	-	-	NH	CCH_3	Br	H	H	Br	Br	H	H	Br

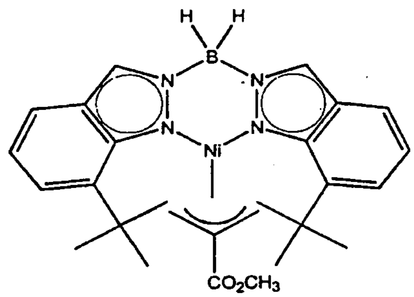
For clarity, the structures of compounds (Ia), (IIb) and (VIa) are shown below;



(Ia),



(IIb), and



(VIa).

In (XXXIII) it is preferred that:

R^{58}, R^{59}, R^{60}, R^{62}, R^{63} and R^{64} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

R^{66} is hydrogen, hydrocarbyl or substituted hydrocarbyl; and

R^{61} and R^{65} are each independently hydrocarbyl containing 2 or more carbon atoms, or substituted hydrocarbyl containing 2 or more carbon atoms.

R^{58}, R^{59}, R^{60}, R^{62}, R^{63} and R^{64} are each hydrogen; and/or

R^{66} is hydrogen; and/or

R^{61} and R^{65} are each independently alkyl, and more preferred that both are isopropyl or methyl.

In a preferred compound or ligand (XVIII) and (XIX):

R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are hydrogen; and/or

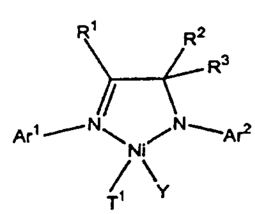
Ar^{10} and Ar^{11} are 2,6-dialkyl substituted phenyl, more preferably 2,6-dimethylphenyl or 2,6-diisopropylphenyl.

Monoanionic ligands which the olefins herein may add to include hydride, alkyl, substituted alkyl, aryl, substituted aryl, or $R^{26}C(=O)-$ wherein R^{26} is hydrocarbyl or substituted hydrocarbyl, and groups π-allyl and π-benzyl groups such as η^3-C_8H_{13}, see for instance J. P. Collman, et al., Principles and Applications of Organotransition Metal Chemistry, University Science Book, Mill Valley, CA, 1987. Such groups are also described in World Patent Application WO 96/23010.

In compound (XXXVI) it is preferred that R^{68} is $-OR^{117}$ or aryl, and/or R^{75} is hydrocarbyl or substituted hydrocarbyl, and/or R^{76} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, more preferably hydrogen, hydrocarbyl or substituted hydrocarbyl.

In the second polymerization process described herein a nickel[II] complex such as any one of (VII)-(XII), (XIX), (XXVIII) or (XXXXI)-(XXXXIV) is either added to the polymerization process or formed in situ in the process. In fact, more than one such complex may be formed during the course of the process, for instance formation of an initial complex and then reaction of that complex to form a living ended polymer containing such a complex.

An example of such a complex which may be formed initially in situ is

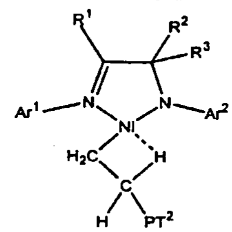


(XV)

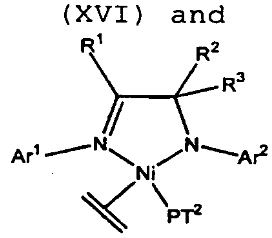
wherein R^1 through R^3, Ar^1 and Ar^2 are as defined above, T^1 is hydride, alkyl, or $R^{42}C(=O)-$ wherein R^{42} is hydrocarbyl or substituted hydrocarbyl or any other

monoanionic ligand which ethylene may add to, and Y is a neutral ligand, or T^1 and Y taken together are a bidentate monoanionic ligand which ethylene may add to. Similar complexes may also be formed with the ligands in (VIII)-(XII), (XIX), (XXVIII) and (XXXXI)-(XXXXIV). Such complexes may be added directly to the process or formed in situ.

After the olefin polymerization has started, the complex may be in forms such as



(XVI) and



(XVII)

wherein R^1 through R^3, Ar^1 and Ar^2 are as defined above, P is a divalent (poly)olefin group [the specific olefin shown in (XVI) and (XVII) is ethylene], $-(CH_2)_x-$ wherein x is an integer of 2 or more, and T^2 is an end group, for example the groups listed for T^1 above. (XVI) is a so-called agostic form complex. Similar complexes may also be formed with the ligands in (VIII)-(XII), (XI), (XXVIII) and (XXXXI)-(XXXXIV). Analogous compounds with other olefins in place of ethylene also may be formed. In all the polymerization processes herein, the temperature at which the olefin polymerization is carried out is about -100°C to about +200°C, preferably about 0°C to about 150°C, more preferably about 25°C to about 100°C. The olefin concentration at which the polymerization is carried out is not critical, atmospheric pressure to about 275 MPa being a suitable range for ethylene and propylene.

The polymerization processes herein may be run in the presence of various liquids, particularly aprotic organic liquids. The catalyst system, olefin, and polyolefin may be soluble or insoluble in these liquids, but obviously these liquids should not prevent the polymerization from occurring. Suitable liquids include alkanes, cycloalkanes, selected halogenated hydrocarbons, and aromatic hydrocarbons. Hydrocarbons are the preferred solvent. Specific useful solvents include hexane, toluene, benzene, chloroform, methylene chloride, 1,2,4-trichorobenzene, p-xylene, and cyclohexane.

The catalysts herein may be "heterogenized" by coating or otherwise attaching them to solid supports, such as silica or alumina. Where an active catalyst species is formed by reaction with a compound such as an alkylaluminum compound, a support on which the alkylaluminum compound is first coated or otherwise attached is contacted with the nickel compound precursor to form a catalyst system in which the active nickel catalyst is "attached" to the solid support. These supported catalysts may be used in polymerizations in organic liquids, as described in the immediately preceding paragraph. They may also be used in so-called gas phase polymerizations in which the olefin(s) being polymerized are added to the polymerization as gases and no liquid supporting phase is present.

Included herein within the definitions of all the polymerization processes are mixtures of starting materials that lead to the formation in situ of the nickel compounds specified in all of the polymerization processes.

In the Examples all pressures are gauge pressures.

Quantitative ^{13}C NMR data for the polymers was obtained using a 10 mm probe on typically 15-20% solutions of the polymer and 0.05M $Cr(acetylacetonate)_3$ in 1,2,4-trichlorobenzene are 120-140°C. For a full

description of determination of branching by ^{13}C and ^{1}H NMR, and for a definition of branches, see World Patent Application 96/23010, which is hereby included by reference.

In the Examples, the following abbreviations are used:

Am - amyl
Bu - butyl
Cy - cyclohexyl
E - ethylene
Et - ethyl
GPC - gel permeation chromatography
Me - methyl
MI - melt index
Mn - number average molecular weight
Mw - weight average molecular weight
MW - molecular weight
N - norbornene
P - propylene
PE - polyethylene
PDI - polydispersity, Mw/Mn
PMAO - poly(methylaluminoxane)
Pr - propyl
RI - refractive index
rt - room temperature
S - styrene
TCB - 1,3,5-trichlorobenzene
THF - tetrahydrofuran
Tm - melting point
tmeda - N,N,N',N'-tetramethylethylenediamine
TO - turnovers, moles of monomer polymerized per mole of catalyst (nickel compound) used

Examples 1-16

Ligand Syntheses

Ligand syntheses and deprotonations were carried out according to the general procedures given below unless stated otherwise. The general procedure for imine synthesis is based upon published procedures for the synthesis of N-aryl-substituted imines given in the following reference: Tom Dieck, H.; Svoboda, M.; Grieser, T. *Z. Naturforsch* **1981**, *36b*, 823 - 832. The synthesis of ArN=CH-CH(*t*-Bu)-N(Ar)(Li) [Ar = 2,6-(*i*-Pr)$_2C_6H_3$] is based on the published synthesis of (*t*-Bu)N=CH-CH(*t*-Bu)-N(*t*-Bu)(Li): Gardiner, M. G.; Raston, C. L. *Inorg. Chem.* **1995**, *34*, 4206 - 4212. The synthesis of ArN=C(Me)-CH=C(Me)-NH(Ar) [Ar = 2,6-(*i*-Pr)$_2C_6H_3$] was published in WO Pat. Appl. 96/23010, and it was deprotonated according to the general procedure given below. The bis(pyrazolyl)borate anions that were used to synthesize complexes 18 and 19 were provided by S. Trofimenko (DuPont) and were synthesized according to the procedures published in the following review: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

General Procedure for Imine Synthesis. In a fume hood, formic acid catalyst was added to a methanol solution of the aldehyde and the aniline (~1.1 - 1.2 equiv). The reaction mixture was stirred and the resulting precipitate was collected on a frit and washed with methanol. The product was then dissolved in Et_2O or CH_2Cl_2 and stirred over Na_2SO_4 overnight. The solution was filtered through a frit with Celite® and the solvent was removed in vacuo to yield the product.

General Procedure for the Synthesis of Sodium Salts. The protonated forms of the ligands were dissolved in anhydrous THF in the drybox. Solid NaH was slowly added to the solution, and then the reaction mixture was stirred overnight. The next day, the solution was filtered through a frit with dry Celite®. The solvent was removed and the resulting powder was

dried in vacuo. With some exceptions (e.g., Example 1), the sodium salts were not soluble in pentane and were further purified by a pentane wash.

Example 1

$ArN{=}C\text{-}CH_2CH_2CH_2\text{-}CH{=}C\text{-}NHAr$ [Ar = 2,6-(i-Pr)$_2C_6H_3$]

A drop of formic acid was added to a solution of 1,2-cyclohexanedione (0.25 g, 2.2 mmol) and 2,6-diisopropylaniline (0.85 mL, 4.5 mmol) in 5 mL of methanol. The reaction mixture was stirred at rt for 3 days. The white solid thus formed was filtered, washed with a small amount of methanol and dried under vacuum. After recrystallization from hot methanol, the product (0.4 g; 41% yield; mp 81-83 $^{\circ}$C) was isolated as white crystals: ^{1}H NMR ($CDCl_3$, 300 MHz, rt): δ 7.28 - 7.08 (m, 6, H_{aryl}), 6.45 (s, 1, N*H*), 4.84 (t, 1, J = 4.6, -C*H*=CNHAr), 3.30 (septet, 2, J = 6.88, C*H*Me_2), 2.86 (septet, 2, J = 6.87, C'*H*Me_2), 2.22 (m, 4, ArN=CCH_2CH_2-), 1.75 (m, 2, CH_2CH=CNHAr), 1.24 and 1.22 (d, 12 each, CHMe_2 and C'HMe_2); ^{13}C NMR ($CDCl_3$, 300 MHz, rt) δ 162.1, 147.3, 145.8, 139.6, 137.0, and 136.4 (ArNH-*C*-*C*=NAr, Ar: C_{ipso}, C_o; Ar': C_{ipso}, C_o), 126.5, 123.4, 123.3 and 122.9 (Ar: C_p, C_m; Ar': C_p, C_m), 106.0 (ArNHC=*C*H-), 29.3, 28.4 and 28.3 (ArNHC=CH-*C*H_2*C*H_2*C*H_2C=NAr), 24.2 and 23.30 (*C*HMe_2, *C'*HMe_2), 23.25 and 22.9 (CHMe_2, C'HMe_2).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): no THF coordinated.

Example 2

ArN=CH-CH(t-Bu)-N(Ar)(Li) [Ar = 2,6-(i-Pr)$_2C_6H_3$]

In a nitrogen-filled drybox, t-BuLi (7.81 mL of a 1.7 M solution in pentane) was filtered through a short plug of dry Celite® into a round bottom flask. The flask was cooled to -35°C in the drybox freezer. The diimine ArN=CH-CH=NAr [Ar = 2,6-(i-Pr_2)C_6H_3] was added as a solid over a period of 15 min to the cold t-BuLi solution. The reaction mixture was stirred for ~2 h to give a viscous red solution. The solution was diluted

with pentane and then filtered through a frit with Celite®. The resulting clear solution was concentrated under vacuum and then cooled in the drybox freezer to $-35^{o}C$. An orange powder was obtained (3.03 g, 51.8%, 1st crop): ^{1}H NMR (THF-d_8, 300 MHz, rt) δ 8.29 (s, 1, C*H*=N), 7.08 (d, 2, J = 7.4, Ar: H_m), 7.00 (t, 1, J = 7.0, Ar: H_p), 6.62 (m, 2, Ar: H_m), 6.14 (t, 1, J = 7.4, Ar: H_p), 4.45 (s, 1, C*H*(*t*-Bu)), 3.08 (br septet, 2, C*H*Me_2), 3.05 (septet, 2, J = 6.8, C*H*Me_2), 1.35 (d, 3, J = 6.7, CH*Me_2*), 1.13 (d, 3, J = 7.0, CH*Me_2*), 1.13 (br s, 12, CH*Me_2*), 1.02 (d, 3, J = 6.7, CH*Me_2*), 0.93 (s, 9, C*Me_3*); ^{13}C NMR (THF-d_8, 75 MHz, rt) δ 184.5 (N=*C*H), 161.9 and 150.1 (Ar, Ar': C_{ipso}), 139.7, 139.5 (br), 139.0 (br) and 137.3 (Ar, Ar': C_o), 125.0, 124.0, 123.5, 122.4 and 112.2 (Ar, Ar': C_m and C_p), 80.8 (*C*H(*t*-Bu)), 41.5 (*C*Me_3), 29.3, 28.6, 27.8 (br), 26.5 (br), 26.3, 25.9, 25.6, 25.0 and 23.3 (br) (Ar, Ar': *CHMe_2; CMe_3*).

Example 3

$[2\text{-(OH)-}3,5\text{-}(t\text{-Bu})_2C_6H_2]\text{-CH=NAr}$ $[Ar = 2,6\text{-}(i\text{-Pr})_2C_6H_3]$

The general procedure for imine synthesis was followed using 10.1 g (43.0 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 9.91 g (55.9 mmol, 1.30 equiv) of 2,6-diisopropylaniline. A light yellow powder (10.5 g, 62.1%) was isolated: ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 13.50 (s, 1, O*H*), 8.35 (s, 1, C*H*=NAr), 7.56 (d, 1, J = 2.7, H_{aryl}), 7.22 (m, 4, H_{aryl}), 3.08 (septet, 2, J = 6.8, C*H*Me_2), 1.55 (s, 9, C*Me_3*), 1.39 (s, 9, C'*Me_3*), 1.23 (d, 12, J = 6.7, CH*Me_2*).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): 0.63 equiv of THF coordinated.

Example 4

[2-(OH)-3,5-(*t*-Bu)$_2$C$_6$H$_2$]-CH=NAr [Ar = 2,6-Me$_2$C$_6$H$_3$]

The general procedure for imine synthesis was followed using 3.05 g (13.0 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 1.89 g (15.6 mmol, 1.20 equiv) of 2,6-dimethylaniline. A yellow powder (2.00 g, 45.6%) was isolated: ^{1}H NMR (CDCl$_3$, 300 MHz, rt, OH resonance not assigned) δ 8.34 (s, 1, C*H*=NAr), 7.50 and 7.16 (d, 1 each, H$_{aryl}$), 7.10 (d, 2, Ar: H$_m$), 7.01 (t, 1, Ar: H$_p$), 2.22 (s, 6, Ar: *Me*), 1.49 (s, 9, C*Me*$_3$), 1.34 (s, 9, C'*Me*$_3$).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-*d*$_8$): 0.51 equiv of THF coordinated.

Example 5

[2-(OH)-3,5-(*t*-Bu)$_2$C$_6$H$_2$]-CH=NAr [Ar = 2,6-Br$_2$-4-F-C$_6$H$_2$]

The general procedure for imine synthesis was followed using 2.12 g (9.05 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 1.89 g (10.8 mmol, 1.20 equiv) of 2,6-dibromo-4-fluoroaniline. A yellow powder (1.11 g, 25.5%) was isolated: ^{1}H NMR (CDCl$_3$, 300 MHz, rt, OH resonance not assigned) δ 8.45 (s, 1, C*H*=NAr), 7.54 (d, 1, H$_{aryl}$), 7.40 (d, 2, J$_{HF}$ ~9, Ar: H$_m$), 7.19 (d, 1, H$_{aryl}$), 1.50 (s, 9, C*Me*$_3$), 1.35 (s, 9, C'*Me*$_3$).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-*d*$_8$): 0.58 equiv of THF coordinated.

Example 6

[2-(OH)-3,5-(NO$_2$)$_2$C$_6$H$_2$]-CH=NAr [Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$]

The general procedure for imine synthesis was followed using 4.98 g (23.5 mmol) of 3,5-dinitro-2-hydroxybenzaldehyde and 4.16 g (23.5 mmol) of 2,6-diisopropylaniline. A yellow powder (6.38 g, 73.1%) was isolated: ^{1}H NMR (CDCl$_3$, 300 MHz, rt, OH resonance not assigned) δ 9.06 (d, 1, H$_{aryl}$), 8.52 (d, 1, H$_{aryl}$), 8.31 (d, 1, J ~ 6, C*H*=NAr), 7.40 (t, 1, Ar:

H_p), 7.30 (d, 2, Ar: H_m), 2.96 (septet, 2, C*H*Me_2), 1.25 (d, 12, CHMe_2).

The sodium salt was cleanly synthesized according to the above general procedure: ^1H NMR (300 MHz, THF-d_8): 0.57 equiv of THF coordinated.

Example 7

[2-(OH)-3,5-$(NO_2)_2C_6H_2$]-CH=NAr [Ar = 2,4,6-(*t*-Bu)$_3C_6H_2$]

The general procedure for imine synthesis was followed using 3.00 g (14.1 mmol) of 3,5-dinitro-2-hydroxybenzaldehyde and 3.88 g (14.9 mmol, 1.06 equiv) of 2,4,6-tris(*t*-butyl)aniline. A yellow powder (4.78 g, 74.5%) was isolated: ^1H NMR ($CDCl_3$, 300 MHz, rt, OH resonance not assigned) δ 9.09 (d, 1, H_{aryl}), 8.41 (d, 1, H_{aryl}), 8.16 (d, 1, J ~ 12, C*H*=NAr), 7.48 (s, 1, Ar: H_m), 1.38 (s, 18, CMe_3), 1.36 (s, 9 C′Me_3).

The sodium salt was cleanly synthesized according to the above general procedure: ^1H NMR (300 MHz, THF-d_8): 2 equiv of THF coordinated.

Example 8

[2-(OH)-3,5-$(NO_2)_2C_6H_2$]-CH=NAr [Ar = 2,6-$Me_2C_6H_3$]

The general procedure for imine synthesis was followed using 3.11 g (14.7 mmol) of 3,5-dinitro-2-hydroxybenzaldehyde and 1.96 g (16.1 mmol, 1.10 equiv) of 2,6-dimethylaniline. A yellow powder (3.63 g, 78.4%) was isolated: ^1H NMR ($CDCl_3$, 300 MHz, rt, OH resonance not assigned) δ 9.05 (d, 1, H_{aryl}), 8.52 (d, 1, H_{aryl}), 8.42 (d, 1, J ~ 9, C*H*=NAr), 7.22 (m, 3, Ar: H_p and H_m), 2.36 (s, 6, Ar: *Me*).

The sodium salt was cleanly synthesized according to the above general procedure: ^1H NMR (300 MHz, THF-d_8): 0.25 equiv of THF coordinated.

Example 9

[2-(OH)-3,5-$(NO_2)_2C_6H_2$]-CH=NAr [Ar = 2,6-Br_2-4-Me-C_6H_2]

The general procedure for imine synthesis was followed using 3.10 g (14.6 mmol) of 3,5-

dinitro-2-hydroxybenzaldehyde and 4.64 g (17.5 mmol, 1.20 equiv) of 2,6-dibromo-4-methylaniline. A yellow powder (5.15 g, ~76.8%) was isolated. The ^1H NMR spectrum of the product showed the presence of methanol, so the powder was dissolved in THF in the drybox under a nitrogen atmosphere and the solution was placed over molecular sieves for several days. The solution was then filtered through a frit with Celite® and the solvent was removed in vacuo: ^1H NMR ($CDCl_3$, 300 MHz, rt; OH resonance not assigned; ~ 1 equiv of THF is present) δ 8.95 (d, 1, J = 2.8, H_{aryl}), 8.76 (s, 1, C*H*=NAr), 8.71 (d, 1, J = 2.8, H_{aryl}), 7.43 (s, 2, Ar: H_m), 2.31 (s, 3, Ar: *Me*).

The sodium salt was cleanly synthesized according to the above general procedure: ^1H NMR (300 MHz, THF-d_8): 3 equiv of THF coordinated.

Example 10

[2-Hydroxynaphthyl]-CH=NAr [Ar = 2,6-(*i*-Pr)$_2C_6H_3$]

The general procedure for imine synthesis was followed using 20.1 g (117 mmol) of 2-hydroxy-1-naphthaldehyde and 24.8 g (140 mmol, 1.20 equiv) of 2,6-diisopropylaniline. A yellow-gold powder (30.8 g, 79.5%) was isolated: ^1H NMR ($CDCl_3$, 300 MHz, rt) δ 15.30 (d, 1, O*H*), 9.15 (d, 1, C*H*=N), 8.08 (d, 1, $H_{naphthyl}$), 7.98 (d, 1, $H_{naphthyl}$), 7.88 (d, 1, $H_{naphthyl}$), 7.60 (t, 1, $H_{naphthyl}$), 7.45 (t, 1, $H_{naphthyl}$), 7.35 (m, 3, Ar: H_m and H_p), 7.29 (d, 1, $H_{naphthyl}$), 3.20 (septet, 2, C*H*Me_2), 1.33 (d, 12, CHMe_2).

The sodium salt was cleanly synthesized according to the above general procedure ^1H NMR (300 MHz, THF-d_8): 0.5 equiv of THF coordinated.

Example 11

[2-Hydroxynaphthyl]-CH=NAr [Ar = 2,6-$Me_2C_6H_3$]

The general procedure for imine synthesis was followed using 33.7 g (196 mmol) of 2-hydroxy-1-naphthaldehyde and 28.4 g (235 mmol, 1.20 equiv) of 2,6-dimethylaniline. A golden yellow powder

(47.2 g, 87.5%) was isolated: ^{1}H NMR ($CDCl_3$, 300 MHz, rt, OH resonance not assigned) δ 9.23 (d, 1, N=C*H*), 8.4 - 7.1 (m, 9, H_{aryl}), 2.41 (s, 6, Ar: *Me*).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): 0.5 equiv of THF coordinated.

Example 12

[2-(OH)-3,5-$Cl_2C_6H_2$]-CH=NAr [Ar = 2,6-(*i*-Pr)$_2C_6H_3$]

The general procedure for imine synthesis was followed using 8.67 g (45.4 mmol) of 3,5-dichloro-2-hydroxybenzaldehyde and 9.66 g (54.5 mmol, 1.20 equiv) of 2,6-diisopropylaniline. A light yellow powder (10.7 g, 67.3%) was isolated: ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 13.95 (s, 1, O*H*), 8.20 (s, 1, C*H*=NAr), 7.50 (d, 1, H_{aryl}), 7.18 - 6.83 (m, 3, H_{aryl}), 7.23 (d, 1, H_{aryl}), 2.89 (septet, 2, C*H*Me_2), 1.16 (d, 12, CH*Me*$_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 165.1 (N=*C*H), 156.1, 145.0, 138.7, 132.9, 129.8, 128.6, 126.2, 123.4, 123.0 and 119.7 (C_{aryl}), 28.3 (*C*HMe$_2$), 23.6 (CH*Me*$_2$).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): 0.5 equiv of THF coordinated.

Example 13

[2-(OH)-3,5-$Cl_2C_6H_2$]-CH=NAr [Ar = 2,6-$Me_2C_6H_3$]

The general procedure for imine synthesis was followed using 16.2 g (85.0 mmol) of 3,5-dichloro-2-hydroxybenzaldehyde and 11.3 g (93.5 mmol, 1.10 equiv) of 2,6-dimethylaniline. A yellow powder (18.2 g, 72.7%) was isolated: ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 14.15 (s, 1, O*H*), 8.43 (s, 1, N=C*H*), 7.65 (d, 1, J = 2.5, H_{aryl}), 7.41 (d, 1, J = 2.5, H_{aryl}), 7.30 - 7.18 (m, 3, Ar: H_m and H_p), 2.35 (s, 6, *Me*).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): 0.33 equiv of THF coordinated.

Example 14

[2-(OH)-5-(NO_2)C_6H_2]-CH=NAr [Ar = 2,6-(*i*-Pr)$_2C_6H_3$]

The general procedure for imine synthesis was followed using 5.22 g (31.2 mmol) of 5-nitro-2-hydroxybenzaldehyde and 6.65 g (37.5 mmol, 1.20 equiv) of 2,6-diisopropylaniline. A yellow powder (4.39 g, 43.1%) was isolated: ^{1}H NMR ($CDCl_3$, 300 MHz, rt, OH resonance not assigned) δ 8.38 (s, 1, C*H*=NAr), 8.35 (d, 1, J = 3, H'_m to hydroxy), 8.30 (dd, 1, J = 9, 3, H_m to hydroxy), 7.23 (s, 3, Ar: H_m and H_p), 7.15 (d, 1, J = 9, H_o to hydroxy), 2.93 (septet, 2, C*H*Me_2), 1.20 (s, 12, CH*Me*$_2$).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): 0.25 equiv of THF coordinated.

Example 15

Pyrrole-2-(CH=NAr) [Ar = 2,6-(*i*-Pr)$_2C_6H_3$]

The general procedure for imine synthesis was followed using 5.00 g (52.6 mmol) of pyrrole-2-carboxaldehyde and 10.3 g (57.9 mmol, 1.1 equiv) of 2,6-diisopropylaniline. The compound was isolated as an off-white powder: ^{1}H NMR ($CDCl_3$, 300 MHz, rt) δ 10.96 (s, 1, N*H*), 8.05 (s, 1, N=C*H*), 7.26 (s, 3, Ar: H_m, H_p), 6.68, 6.29 and 6.24 (m, 1 each, $H_{pyrrole}$), 3.17 (septet, 2, J = 6.9, C*H*Me_2), 1.20 (d, 12, J = 7.2, CH*Me*$_2$); ^{13}C NMR ($CDCl_3$, 75 MHz, rt) δ 152.6 (N=*C*H), 148.5, 138.9 and 129.9 (pyrrole: C_{ipso}; Ar: C_{ipso}, C_o), 124.5, 124.0, 123.2, 116.5 and 109.9 (pyrrole: 3 CH carbons and Ar: C_m, C_p), 27.9 (*C*HMe_2), 23.6 (CH*Me*$_2$).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, C_6D_6/THF-d_8): 1 equiv of THF coordinated.

Example 16

(Ar)(H)N-C(Me)=CH-C(O)OMe [Ar = 2,6-(*i*-Pr)$_2C_6H_3$]

Concentrated HCl (2 drops) was added to a solution of methylacetoacetate (5.2 mL; 48.5 mmol) and 2,6-diisopropylaniline (8.58 g, 48.5 mmol) in methanol.

The reaction mixture was stirred at room temperature for 30 h. The product (5.95 g; 45% yield; mp 125-127^{O}C) was filtered, washed with a small amount of methanol, and then dried under vacuum. Additional product (3.79 g, 28%; mp 115-122^{O}C) was isolated from the mother liquor: ^{1}H NMR (300 MHz, $CDCl_3$, rt): δ 9.78 (br s, 1, N*H*), 7.29 (t, 1, J = 8.1, Ar: H_p), 7.17 (d, 2, J = 8.2, Ar: H_m), 4.71 (s, 1, =C*H*), 3.70 (s, 3, OMe), 3.10 (septet, 2, J = 6.8, C*H*Me_2), 1.61 (s, 3, =C*Me*), 1.22 (d, 6, J = 6.8, CH*Me*Me'), 1.1.5 (d, 6, J = 6.7, CHMe*Me'*).

The sodium salt was cleanly synthesized according to the above general procedure: ^{1}H NMR (300 MHz, THF-d_8): no THF coordinated.

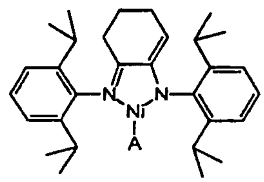
Examples 17 - 40

Synthesis of Nickel Complexes

General Synthesis of Nickel Allyl Initiators. A mixture of two equiv of the appropriate anionic ligand and one equiv of $[(allyl)Ni(\mu\text{-}X)]_2$ (X = Cl or Br) was dissolved in THF. The reaction mixture was stirred for several h before being filtered. The solvent was removed in vacuo to yield the desired product. Depending on the solubility of the product, further purification was often carried out by dissolving the product in Et_2O or pentane and filtering again or washing the product with Et_2O or pentane. Due to ease of characterization and, especially, ease of initiation in the presence of a Lewis acid, typically allyl = (a) $H_2CC(CO_2Me)CH_2$. However, other allyl derivatives were also synthesized and their polymerization activity explored; these include allyl = (b) H_2CCHCH_2, (c) $H_2CCHCHMe$, (d) $H_2CCHCMe_2$, (f) $H_2CCHCHCl$, and (g) $H_2CCHCHPh$. The $[(allyl)Ni(\mu\text{-}X)]_2$ precursors were synthesized according to the procedures published in the following reference: Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, D.;

Zimmermann, H. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 151-164.

Complexes **1 - 20** were synthesized according to the above general procedure and their structures, syntheses and characterization follow:



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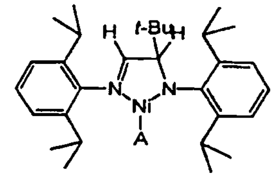

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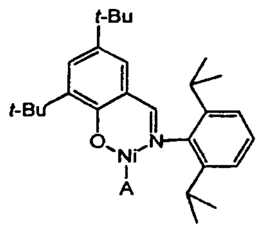

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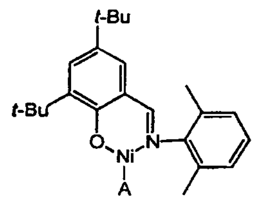

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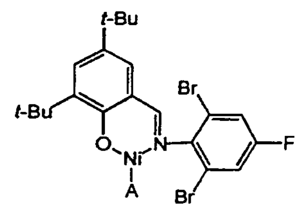

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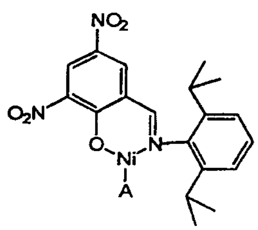

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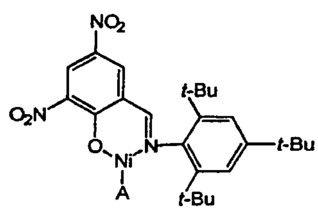

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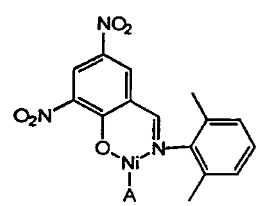

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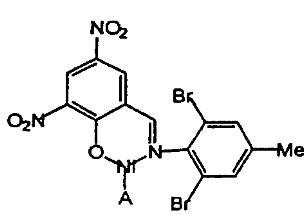

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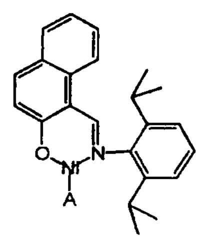

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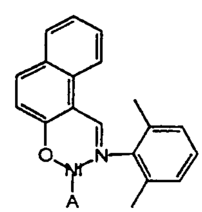

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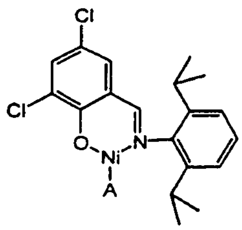

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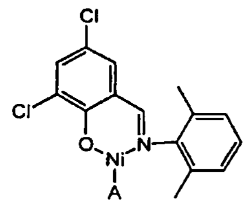

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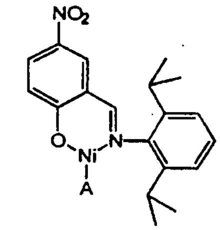

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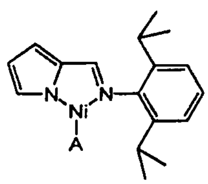

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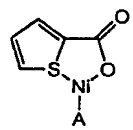

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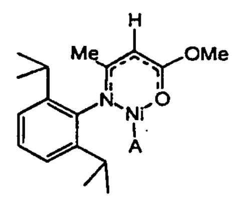

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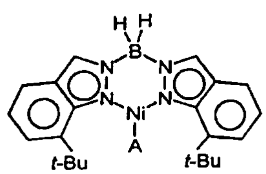

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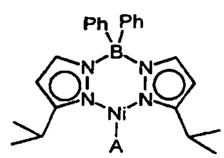

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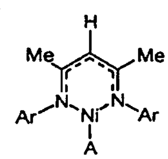
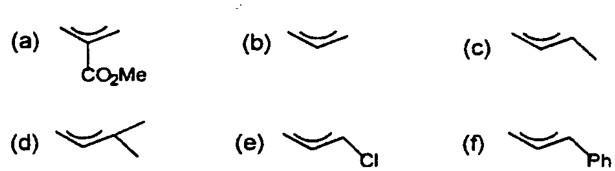


Ar = 2,6-(i-Pr_2)C_6H_3

20

A (Allyl)



Example 17

Complex 1a. Two equiv (610 mg, 1.35 mmol) of the sodium salt of the ligand were reacted with one equiv (321 mg, 0.674 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 655 mg (82.6% yield) of a deep purple powder.

Example 18

Complex 1d. Two equiv (667 mg, 1.47 mmol) of the sodium salt of the ligand were reacted with one equiv (306 mg, 0.737 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CCHCMe_2$) to give a purple solid: ^1H NMR (C_6D_6, 300 MHz, rt, H_2CCHCMe$_2$ resonances not assigned) δ 7.25 - 6.79 (m, 6, H_{aryl}), 4.93 (t, 1, J = 4.6, ArNHC=C*H*-), 4.56 (br m, 1, H_2CC*H*CMe$_2$), 3.48 (septet, 2, J = 6.9, C*H*Me$_2$), 2.99 (septet, 2, J = 6.9, C'*H*Me$_2$), 2.07 (m, 2, Cy: CH_2), 1.92 (m, 2, Cy: CH_2), 1.42 (m, 2, Cy: CH_2), 1.2 - 1.1 (doublets, 24, C*H*Me$_2$, C'*H*Me$_2$), 0.72 and 0.61 (br s, 3 each, H_2CCHC*MeMe'*).

Example 19

Complex 2a. Two equiv (1.08 g, 2.44 mmol) of the lithium salt of the ligand were reacted with one equiv (581 mg, 1.22 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to yield 1.35 g (93.8% yield) of a red powder. ^1H NMR spectrum in C_6D_6 is complex.

Example 20

Complex 3a. Two equiv (4.01 g, 8.71 mmol) of the sodium salt of the ligand were reacted with one equiv (2.07 g, 4.35 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to yield 3.61 g (75.2% yield) of a golden yellow powder. ^1H NMR (C_6D_6, 300 MHz, rt) δ 7.84 (s, 1, N=C*H*), 7.44 and 6.92 (d, 1 each, H_{aryl}), 7.20 (m, 3, Ar: H_m, H'_m and H_p), 3.88 (d, 1, *H*H'CC(CO$_2$Me)CHH'), 3.86 (septet, 1, C*H*Me$_2$), 3.80 (s, 3, OMe), 3.04 (septet, 1, C'*H*Me$_2$), 2.91 (s, 1, HH'CC(CO$_2$Me)C*H*H'), 1.89 (m, 1, H*H'*CC(CO$_2$Me)CHH'), 1.43 (s, 1, HH'CC(CO$_2$Me)CH*H'*), 1.41 and 1.25 (s, 9 each, C*Me$_3$* and C'*Me$_3$*), 1.37, 1.27, 1.16 and 1.02 (d, 3 each, CH*MeMe'* and C'H*MeMe'*); ^{13}C NMR (CD_2Cl_2, 75 MHz, rt) δ

166.6 (N=*C*H), 167.4, 164.7, 153.0, 141.3, 140.9, 139.9, 136.5, 117.7 and 110.9 (H_2C*C*(*C*O_2Me)CH_2; Ar: C_{ipso}, C_o, C'_o; Ar': C_{ipso}, C_o, C_m, C'_m), 130.2, 127.9, 126.8, 124.0 and 123.9 (Ar: C_m, C'_m, C_p; Ar': C_p and C'_o), 59.8 and 47.0 (H_2*C*C(CO_2Me)*C*H_2), 53.1 (CO_2*Me*), 35.9 and 34.3 (*C*Me_3 and *C'*Me_3), 31.6 and 30.0 (CMe_3 and C'Me_3), 29.0, 28.5, 25.7, 25.6, 23.3 and 22.7 (CH*MeMe'* and C'H*MeMe'*).

Single crystals were formed by cooling a pentane solution of the complex to -35°C in the drybox freezer. The structure of the compound was solved by X-ray crystallography and is in agreement with the proposed structure.

Example 21

Complex 4a. Two equiv (834 mg, 2.11 mmol) of the sodium salt of the ligand were reacted with one equiv (501 mg, 1.05 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 935 mg (89.7% yield) of a golden yellow powder: ^{1}H NMR (THF-d_8, 300 MHz, rt) δ 7.94 (s, 1, N=C*H*), 7.40 (d, 1, H_{aryl}), 7.13 - 6.92 (m, 3, Ar: H_m, H'_m, H_p), 7.00 (d, 1, H_{aryl}), 3.78 (s, 3, OMe), 3.76 (d, 1, *H*H'CC(CO_2Me)CHH'), 2.80 (s, 1, HH'CC(CO_2Me)C*H*H'), 2.45 (s, 3, Ar: *Me*), 2.10 (s, 3, Ar: *Me'*), 1.85 (d, 1, H*H'*C(CO_2Me)CHH'), 1.60 (t, 1, HH'CC(CO_2Me)CH*H'*), 1.40 and 1.24 (s, 9 each, CMe_3 and C'Me_3); ^{13}C NMR (CD_2Cl_2, 75 MHz, rt) δ 166.2 (N=*C*H), 167.3, 164.3, 155.1, 141.1, 136.2, 130.0, 129.4, 118.0 and 110.3 (H_2C*C*(*C*O_2Me)CH_2, Ar: C_{ipso}, C_o, C'_o; Ar': C_{ipso}, C_o, C_m, C'_m), 129.8, 128.5, 128.4, 127.8 and 125.6 (Ar: C_m, C'_m, C_p; Ar': C_p, C'_o), 57.8 and 47.7 (H_2*C*C(CO_2Me)*C*H_2), 52.8 (OMe), 35.7 and 34.1 (*C*Me_3 and *C'*Me_3), 31.4 and 29.4 (CMe_3 and C'Me_3), 19.0 and 18.4 (Ar: *Me* and *Me'*).

Example 22

Complex 5a. Two equiv (390 mg, 0.709 mmol) of the sodium salt of the ligand were reacted with one equiv (169 mg, 0.355 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 189 mg (45.8% yield) of a

golden yellow powder: ^1H NMR ($CDCl_3$, 300 MHz, rt, broad resonances) δ 7.80 (br s, 1, N=C*H*), 7.50 (br s, 1, H_{aryl}), 7.42 (br s, 1, Ar: H_m, H'_m), 6.96 (br s, 1, H_{aryl}), 3.92 (br s, 1, *H*H'CC(CO_2Me)CHH'), 3.86 (br s, 3, OMe), 2.84 (br s, 1, HH'CC(CO_2Me)C*H*H'), 1.98 and 1.76 (br s, 1 each, H*H'*CC(CO_2Me)CH*H'*), 1.43 and 1.29 (br s, 9 each, C*Me3* and C'*Me3*).

Example 23

Complex 6a. Two equiv (900 mg, 2.10 mmol) of the sodium salt of the ligand were reacted with one equiv (500 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 864 mg (77.9% yield) of a golden yellow powder: ^1H NMR (C_6D_6, 300 MHz, rt) δ 8.40 (d, 1, J = 3.0, H_{aryl}), 7.66 (d, 1, J = 3.0, H_{aryl}), 7.12 (s, 1, N=C*H*), 7.10 - 6.90 (m, 3, Ar: H_m, H'_m, H_p), 4.05 (m, 1, *H*H'CC(CO_2Me)CHH'), 3.49 (septet, 1, J = 6.9, C*H*Me_2), 3.21 (s, 3, OMe), 2.96 (septet, 1, J = 6.8, C'*H*Me_2), 2.67 (s, 1, HH'CC(CO_2Me)C*H*H'), 2.23 (m, 1, H*H'*CC(CO_2Me)CHH'), 1.34 (br s, 1, HH'CC(CO_2Me)CH*H'*), 1.36, 1.15, 0.95 and 0.84 (d, 3 each, J = 6.8, CH*MeMe'*, C'H*MeMe'*).

Example 24

Complex 6f. Two equiv (267 mg, 0.621 mmol) of the sodium salt of the ligand were reacted with one equiv (105 mg, 0.310 mmol) of [(allyl)Ni(μ-Cl)]$_2$ (allyl = $H_2CCHCHCl$) to give 245 mg (78.3% yield) of a golden yellow powder: ^1H NMR spectrum in C_6D_6 is complex.

Example 25

Complex 7a. Two equiv (926 mg, 1.49 mmol) of the sodium salt of the ligand were reacted with one equiv (354 mg, 0.745 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 861 mg (94.4% yield) of a golden yellow powder: ^1H NMR (C_6D_6, 300 MHz, rt) δ 8.43 (d, 1, J = 2.6, H_{aryl}), 7.81 (d, 1, J = 2.9, H_{aryl}), 7.48 (s, 2, Ar: H_m), 7.45 (s, 1 , N=C*H*), 4.12 (d, 1, J = 2.9, *H*H'C(CO_2Me)CHH'), 3.28 (s, 3, O*Me*), 2.84 (s, 1, HH'C(CO_2Me)C*H*H'), 2.44 (t, 1, J = 2.4, H*H'*C(CO_2Me)CHH'), 1.58, 1.41 and 1.28 (s, 9 each, C*Me3*,

C'*Me*$_3$, C''*Me*$_3$), 1.31 (d, 1, J = 1.1, HH'C(CO$_2$Me)CH*H'*); ^{13}C NMR (C_6D_6, 75 MHz, rt) δ 166.4 (N=*C*H), 165.5, 162.9, 151.0, 148.1, 144.9, 139.4, 138.8, 134.21, 120.5 and 113.4 (H$_2$C*C*(*C*O$_2$Me)CH$_2$; Ar: C$_{ipso}$, C$_o$, C'$_o$, C$_p$; Ar': C$_{ipso}$, C$_o$, C$_m$, C'$_m$), 134.16, 126.1, 125.1 and 124.7 (Ar: C$_m$, C'$_m$ and Ar': C$_p$ and C'$_o$), 63.3 and 49.0 (H$_2$*C*(CO$_2$Me)*C*H$_2$), 52.4 (OMe), 37.2 (*C*Me$_3$), 34.8, 34.4 and 31.4 (C*Me*$_3$, C'*Me*$_3$ and C''*Me*$_3$), (*C'*Me$_3$ and *C''*Me$_3$ overlap with *C*Me$_3$ or C*Me*$_3$ or C'*Me*$_3$ resonances).

Example 26

Complex 8a. Two equiv (529 mg, 1.49 mmol) of the sodium salt of the ligand were reacted with one equiv (354 mg, 0.745 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H$_2$CC(CO$_2$Me)CH$_2$) to give 662 mg (94.1% yield) of a golden yellow powder: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) δ 8.80 (d, 1, H$_{aryl}$), 8.40 (d, 1, H$_{aryl}$), 8.08 (s, 1, N=C*H*), 7.14 (m, 3, Ar: H$_m$, H'$_m$, H$_p$), 3.82 (d, 1, *H*H'CC(CO$_2$Me)CHH'), 3.88 (s, 3, OMe), 3.00 (s, 1, HH'C(CO$_2$Me)C*H*H'), 2.46 (s, 3, Ar: *Me*), 2.16 (m, 1, H*H'*CC(CO$_2$Me)CHH'), 2.14 (s, 3, Ar: *Me'*), 1.91 (s, 1, HH'CC(CO$_2$Me)CH*H'*).

Example 27

Complex 9a. Two equiv (1.46 g, 2.09 mmol) of the sodium salt of the ligand were reacted with one equiv (497 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H$_2$CC(CO$_2$Me)CH$_2$) to give 1.42 g (96.0% yield) of a red powder: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) δ 8.79 (d, 1, H$_{aryl}$), 8.44 (d, 1, H$_{aryl}$), 8.06 (s, 1, N=C*H*), 7.51 and 7.49 (s, 1 each, Ar: H$_m$, H'$_m$), 3.96 (d, 1, *H*H'CC(CO$_2$Me)CHH'), 3.85 (s, 3, OMe), 3.65 (br s, ~ 1.25 equiv THF), 3.00 (s, 1, HH'CC(CO$_2$Me)C*H*H'), 2.37 (s, 3, Ar: *Me*), 2.23 (m, 1, H*H'*CC(CO$_2$Me)CHH'), 2.13 (s, 1, HH'CC(CO$_2$Me)CH*H'*), 1.85 (br s, ~ 1.25 equiv THF); ^{13}C NMR (CD$_2$Cl$_2$, 75 MHz, rt) δ 168.3 (N=*C*H), 166.0, 163.6, 148.9, 142.7, 140.5, 134.3, 122.0, 117.3, 116.7 and 114.8 (H$_2$C*C*(*C*O$_2$Me)CH$_2$; Ar: C$_{ipso}$, C$_o$, C'$_o$, C$_p$; Ar': C$_{ipso}$, C$_o$, C$_m$, C'$_m$), 136.1, 133.5, 133.5 and 126.3 (Ar: C$_m$, C'$_m$; Ar': C$_p$, C'$_o$); 72.6 (br, THF), 61.2 and 51.4

($H_2CC(CO_2Me)CH_2$), 53.6 (OMe), 34.9 (br, THF), 20.8 (Ar: *Me*).

Example 28

Complex 10a. Two equiv (490 mg, 1.3 mmol) of the sodium salt of the ligand were reacted with one equiv (300 mg, 0.63 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 259 mg (~41% yield) of a yellow-green powder. About 12.5% of the isolated sample consists of a second species whose NMR spectrum is consistent with a $(ligand)_2Ni(II)$ complex. The remainder is the allyl complex: ^1H NMR (C_6D_6, 300 MHz, rt) δ 8.75 (s, 1, N=C*H*), 7.50 - 6.90 (m, 8, H_{aryl}), 6.03 (d, 1, J = 9.2, H_{aryl}), 4.16 (d, 1, J = 3.0, *H*H'CC(CO_2Me)CHH'), 3.92 (septet, 1, J = 6.9, C*H*Me_2), 3.33 (s, 3, OMe), 3.27 (septet, 1, J = 6.8, C'*H*Me_2), 2.83 (s, 1, HH'CC(CO_2Me)C*HH'*), 2.77 (dd, 1, J = 3.4, 1.6, H*H'*CC(CO_2Me)CHH'), 1.47 (dd, 1, J = 1.5, 0.9, HH'CC(CO_2Me)CH*H'*), 1.36, 1.20, 1.02 and 0.92 (d, 3 each, J = 6.5 - 6.8, CH*MeMe'*, C'H*MeMe'*). [Proposed $(ligand)_2Ni(II)$ complex: δ 8.19 (s, 2, N=C*H*), 7.50 - 6.90 (m, 16, H_{aryl}), 6.12 (d, 2, H_{aryl}), 4.54 (septet, 4, J = 6.98, C*H*Me_2), 1.53 (d, 12, J = 6.8 CH*Me*Me'), 1.18 (d, 12, CHMe*Me'*).]

Example 29

Complex 11a. Two equiv (487 mg, 1.32 mmol) of the sodium salt of the ligand were reacted with one equiv (314 mg, 0.660 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 351 mg (~61.5% yield) of a yellow-green powder. About 17% of the isolated product consists of a second species whose NMR spectrum is consistent with a $(ligand)_2Ni(II)$ complex; the remainder is the allyl complex: ^1H NMR (C_6D_6, 300 MHz, rt) δ 8.64 (s, 1, N=C*H*), 7.41 - 6.93 (m, 8, H_{aryl}), 6.05 (d, 1, J = 9.2, H_{aryl}), 4.07 (d, 1, J = 3.3, *H*H'CC(CO_2Me)CHH'), 3.30 (s, 3, OMe), 2.65 (s, 1, HH'CC(CO_2Me)C*HH'*), 2.28 (s, 3, Ar: *Me*), 2.16 (s, 4, Ar: *Me'* and H*H'*CC(CO_2Me)CHH'), 1.41 (br s, 1,

HH'CC(CO_2Me)CH*H'*. [Proposed (ligand)$_2$Ni complex: δ 8.01 (s, 2, N=C*H*), 2.66 (s, 12, Ar: *Me*).]

Example 30

Complex 11b. Two equiv (179 mg, 0.484 mmol) of the sodium salt of the ligand were reacted with one equiv (101 mg, 0.242 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H_2CCHCMe$_2$) to give an orange-yellow powder (176 mg, 90.4%): ^{1}H NMR (C_6D_6, 300 MHz, rt) δ 8.65 (s, 1, N=C*H*), 7.48 - 6.94 (m, 9, H_{aryl}), 5.14 (dd, 1, J = 13.0, 7.9, H_2CC*H*CMe$_2$), 2.34 (s, 3, Ar: *Me*), 2.08 (s, 3, Ar: *Me'*), 1.40 (d, 1, J = 7.7, *H*H'CCHCMe$_2$), 1.36 (d, 1, J = 13.1, H*H'*CCHCMe$_2$), 1.13 and 1.02 (s, 3 each, H_2CCHC*MeMe'*).

Example 31

Complex 12a. Two equiv (862 mg, 2.11 mmol) of the sodium salt of the ligand were reacted with one equiv (501 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H_2CC(CO_2Me)CH$_2$) to give 951 mg (~88.8% yield) of a yellow-green powder. About 10% of the isolated product consists of a second species whose NMR spectrum is consistent with a (ligand)$_2$Ni(II) complex; the remainder is the allyl complex: ^{1}H NMR (C_6D_6, 300 MHz, rt) δ 7.40 (s, 1, N=C*H*), 7.38 - 6.98 (m, 5, H_{aryl}), 4.13 (d, 1, J = 2.9, *H*H'CC(CO_2Me)CHH'), 3.61 (septet, 1, J = 6.9, C*H*Me$_2$), 3.27 (s, 3, OMe), 3.03 (septet, 1, J = 6.8, C'*H*Me$_2$), 2.78 (s, 1, HH'CC(CO_2Me)C*H*H'), 2.16 (t, 1, J = 1.7, H*H'*CC(CO_2Me)CHH'), 1.38 (br s, 1, HH'CC(CO_2Me)C*H*H'), 1.34, 1.16, 0.94 and 0.83 (d, 3 each, J = 6.6 - 7.0, CH*MeMe'*, C'H*MeMe'*); ^{13}C NMR (C_6D_6, 75 MHz, rt, diagnostic resonances) δ 165.2 (N=*C*H), 61.9 and 48.7 (H_2*C*C(CO_2Me)*C*H$_2$), 52.3 (OMe), 28.7 and 28.4 (*C*HMe$_2$; *C'*HMe$_2$), 25.3, 25.3, 22.8 and 22.6 (CH*MeMe'*, C'H*MeMe'*). [Proposed (ligand)$_2$Ni complex: ^{1}H NMR (C_6D_6) δ 7.20 - 6.36 (m, 12, N=C*H* and H_{aryl}), 4.49 (septet, 4, J = 6.9, C*H*Me$_2$), 1.42 and 1.13 (d, 12 each, J = 7.0, CH*MeMe'*); ^{13}C NMR (C_6D_6) δ 29.6: (*C*HMe$_2$), 24.4 and 23.6 (CH*MeMe'*).]

Example 32

Complex 13a. Two equiv (491 mg, 1.26 mmol) of the sodium salt of the ligand were reacted with one equiv (300 mg, 0.632 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 469 mg (~82.4% yield) of a green powder. ~13% of the isolated product consists of a second species whose NMR spectrum is consistent with a (ligand)$_2$Ni(II) complex; the remainder is the allyl complex: ^{1}H NMR (C_6D_6, 300 MHz, rt) δ 7.37 (d, 1, J = 2.6, H_{aryl}), 6.98 (s, 1, N=C*H*), 6.98 - 6.86 (m, 3, H_{aryl}), 6.56 (d, 1, J = 2.0, H_{aryl}), 4.05 (d, 1, J = 2.6, *H*H'CC(CO_2Me)CHH'), 3.23 (s, 3, OMe), 2.60 (s, 1, HH'CC(CO_2Me)C*H*H', overlaps with Ar: Me of dimer), 2.09 and 2.03 (s, 3 each, Ar: *Me*, *Me'*), 2.06 (m, 1, H*H'*CC(CO_2Me)CHH'), 1.31 (s, 1, HH'CC(CO_2Me)CH*H'*). [Proposed (ligand)$_2$Ni(II) complex: δ 2.60 (s, Ar: Me).]

Example 33

Complex 14a. Two equiv (772 mg, 2.11 mmol) of the sodium salt of the ligand were reacted with one equiv (501 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 891 mg (87.4% yield) of a yellow-orange powder: ^{1}H NMR (CD_2Cl_2, 300 MHz, rt) δ 8.25 (d, 1, Ar': H_o), 8.16 (dd, 1, Ar': H_p), 7.98 (s, 1, N=C*H*), 7.24 (m, 3, Ar: H_m, H'_m, H_p), 6.90 (d, 1, Ar': H_m), 3.92 (d, 1, *H*H'CC(CO_2Me)CHH'), 3.86 (s, 3, OMe), 2.99 (septet, 1, C*H*Me_2), 3.02 (s, 1, HH'CC(CO_2Me)C*H*H'), 2.98 (septet, 1, C'*H*Me_2), 2.08 (m, 1, H*H'*CC(CO_2Me)CHH'), 1.66 (t, 1, HH'CC(CO_2Me)CH*H'*), 1.39, 1.31, 1.17 and 1.01 (d, 3 each, CH*MeMe'* and C'H*MeMe'*).

Example 34

Complex 15a. Two equiv (1.09 g, 3.13 mmol) of the sodium salt of the ligand were reacted with one equiv (743 mg, 1.56 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 858 mg (66.7% yield) of a yellow-orange powder: ^1H NMR (C_6D_6, 300 MHz, rt) δ 7.20 - 7.00 (m, 5, N=C*H*; Ar: H_m, H'_m, H_p; $H_{pyrrole}$), 6.77 (m, 1, $H_{pyrrole}$), 6.42 (m, 1, $H_{pyrrole}$), 3.84 (m, 1, *H*H'CC(CO_2Me)CHH'), 3.65 (septet, 1, J = 6.8, C*H*Me_2), 3.30 (s, 3, OMe), 3.19 (septet, 1, J = 6.9, C'*H*Me_2), 2.85 (m, 1, HH'CC(CO_2Me)C*H*H'), 2.20 (d, 1, J = 0.89, *H*H'CC(CO_2Me)CHH'), 1.89 (d, 1, J = 0.89, H*H'*CC(CO_2Me)CHH'), 1.24, 1.18, 1.05 and 0.92 (d, 3 each, J = 6.8 - 7.1, CH*MeMe'*, C'H*MeMe'*); ^{13}C NMR (C_6D_6, 75 MHz, rt) δ 162.5 (N=*C*H), 166.2, 148.7, 141.5, 141.4, 141.3, 140.8, 126.5, 123.43, 123.39, 118.8, 114.0 and 109.6 (H_2C*C*(*C*O_2Me)CH_2); C_{aryl}; $C_{pyrrole}$), 54.0 and 50.3 (H_2*C*C(CO_2Me)*C*H_2), 52.1 (OMe), 28.4 and 28.3 (*C*HMe_2, *C'*HMe_2), 25.1, 24.9, 23.0 and 22.5 (CH*MeMe'* and C'H*MeMe'*).

Example 35

Complex 16a. Two equiv (323 mg, 2.15 mmol) of the sodium salt of the ligand were reacted with one equiv (511 mg, 1.07 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 322 mg (62.6% yield) of an off-white (slightly red) powder.

Example 36

Complex 17a. Two equiv (987 mg, 3.32 mmol) of the sodium salt of the ligand were reacted with one equiv (789 mg, 1.66 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 1.14 g (79.4% yield) of a bright yellow-orange powder: ^1H NMR (C_6D_6, 300 MHz, rt) δ 7.06 (br s, 3, H_{aryl}), 4.86 (d, 1, J = 1.2, ArNC(Me)C*H*CO_2Me), 4.04 (septet, 1, J = 6.7, C*H*Me_2), 3.90 (d, 1, J = 3.0, *H*H'CC(CO_2Me)CHH'), 3.37 and 3.36 (s, 3 each, $(OMe)_{allyl}$ and $(OMe)_{ligand}$), 3.24 (septet, 1, J = 7.0, C'*H*Me_2), 2.66 (s, 1, HH'CC(CO_2Me)C*H*H'), 2.01 (m, 1, H*H'*CC(CO_2Me)CHH'), 1.44 (s, 3,

ArNC(*Me*)CHCO$_2$Me), 1.36, 1.29, 1.17 and 1.03 (d, 3 each, J = 6.2 - 6.9, CH*MeMe'*, C'H*MeMe'*), 1.14 (br s, 1, HH'CC(CO$_2$Me)CH*H'*); ^{13}C NMR (C$_6$D$_6$, 75 MHz, rt) δ 170.5, 169.4, 166.7, 151.5, 147.3, 141.1, 140.1, 125.4, 123.7 and 109.2 (Ar: C_{ipso}, C_o, C_o', C_m, C_m', C_p; H$_2$C*C*(*C*O$_2$Me)CH$_2$; ArN*C*(Me)CH*C*O$_2$Me), 80.2 (ArNC(Me)*C*HCO$_2$Me), 60.8 and 46.3 (H$_2$*C*C(CO$_2$Me)*C*H$_2$), 52.0 and 50.9 (H$_2$CC(CO$_2$*Me*)CH$_2$, ArNC(Me)CHCO$_2$*Me*), 28.4 and 28.1 (*C*HMe$_2$, *C'*HMe$_2$), 24.5, 24.3, 24.3 and 23.6 (CH*MeMe'*, C'H*MeMe'*), 23.2 (ArNC(*Me*)CHCO$_2$Me).

Example 37

Complex 18a. Two equiv (1.20 g, 2.14 mmol) of the thallium salt of the ligand were reacted with one equiv (508 mg, 1.07 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H$_2$CC(CO$_2$Me)CH$_2$) to give 730 mg (72.2% yield) of a red powder: ^{1}H NMR spectrum in C$_6$D$_6$ is complex.

Example 38

Complex 19a. Two equiv (435 mg, 1.03 mmol) of the potassium salt of the ligand were reacted with one equiv (245 mg, 0.514 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H$_2$CC(CO$_2$Me)CH$_2$) to give 309 mg (60.4% yield) of a golden yellow powder. Some impurities are present, but the majority of the product is the allyl complex: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, rt) δ 7.44 (s, 2, $H_{pyrazole}$), 7.4 - 7.0 (m, 10, H_{aryl}), 6.00 (s, 2, $H_{pyrazole}$), 3.91 (s, 3, OMe), 3.50 (s, 2, *H*H'CC(CO$_2$Me)C*H*H'), 2.96 (septet, 2, J = 6.8, C*H*Me$_2$), 1.27 (d, 6, J = 7.0, CH*Me*Me'), 1.19 (d, 6, J = 7.0, CHMe*Me'*), 0.90 (s, 2, H*H'*CC(CO$_2$Me)CH*H'*).

Example 39

Complex 20a. Two equiv (583 mg, 1.32 mmol) of the sodium salt of the ligand were reacted with one equiv (315 mg, 0.662 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = H$_2$CC(CO$_2$Me)CH$_2$) to give 407 mg (53.6% yield) of a bright yellow-green powder: ^{1}H NMR (C$_6$D$_6$, 300 MHz, rt) δ 7.11 (m, 6, H_{aryl}), 5.04 (s, 1, NC(Me)C(*H*)C(Me)N), 4.04 (septet, 2, C*H*Me$_2$), 3.40 (septet, 2, C'*H*Me$_2$), 3.35 (s, 3, OMe), 2.29 (s, 2, *H*H'CC(CO$_2$Me)C*H*H'), 1.95 (s, 2,

$HH'CC(CO_2Me)CHH'$), 1.62 (s, 6, NC(*Me*)C(H)C(*Me*)N), 1.38, 1.32, 1.20 and 1.07 (d, 6 each, CH*MeMe'*, C'H*MeMe'*).

Example 40

Complex 20b. Two equiv (296 mg, 0.672 mmol) of the sodium salt of the ligand were reacted with one equiv (90.8 mg, 0.336 mmol) of $[(allyl)Ni(\mu\text{-}Cl)]_2$ (allyl = H_2CCHCH_2) to give 151 mg (43.4% yield) of a bright yellow-orange powder: ^1H NMR (C_6D_6, 300 MHz, rt) δ 7.14 - 7.02 (m, 6, H_{aryl}), 5.84 (m, 1, $H_2CC\mathit{H}CH_2$), 5.04 (s, 1, NC(Me)C(*H*)C(Me)N), 4.05 (septet, 2, J = 6.9, C*H*Me$_2$), 3.43 (septet, 2, J = 6.9, C'*H*Me$_2$), 1.79 (d, 2, J = 12.8, *H*H'CCHC*H*H'), 1.64 (s, 6, NC(*Me*)C(H)C(*Me*)N), 1.53 (d, 2, J = 6.8, H*H'*CCHCH*H'*), 1.39 1.29, 1.21 and 1.10 (d, 6 each, J = 6.8 - 7.1, CH*MeMe'*, C'H*MeMe'*).

Examples 41 - 130

Ethylene and Propylene Polymerization Procedures and Reactions

The results of ethylene and propylene polymerizations catalyzed by complexes **1-20** under various reaction conditions (see general procedures and Table 1 below) are reported in Tables 2-5. The polymers were characterized by NMR, GPC, and DSC analysis. A description of the methods used to analyze the amount and type of branching in polyethylene samples by ^{13}C NMR spectroscopy is given in WO Pat. Appl. 96/23010. GPC's were run in trichlorobenzene at 135°C and calibrated against polystyrene standards.

General Procedure for the Screening of Ethylene Polymerizations by Nickel Allyl Initiators at 6.9 MPa Ethylene.

In the drybox, a glass insert was loaded with the isolated allyl initiator. The insert was cooled to -35°C in the drybox freezer, 5 mL of solvent (typically C_6D_6 or $CDCl_3$) was added to the cold insert, and the insert was cooled again. A Lewis acid cocatalyst [typically BPh_3 or $B(C_6F_5)_3$] was often added to the cold solution, and the insert was then capped and

sealed. Outside of the drybox, the cold tube was placed under ethylene (typically 6.9 MPa) and allowed to warm to rt as it was shaken mechanically for approximately 18 h. An aliquot of the solution was used to acquire a ^1H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

General Procedure for the Screening of Ethylene Polymerizations by Nickel Allyl Initiators at 28-35 kPa Ethylene with Polymethylaluminoxane (PMAO) Cocatalyst.

In the drybox, the nickel complex was placed in a Schlenk flask and dissolved in ~ 20 mL of toluene. The flask was sealed, removed from the drybox and attached to an ethylene line where it was purged with first nitrogen and then ethylene. After purging with ethylene, PMAO was quickly added to the reaction mixture and the flask was placed under 28-35 kPa of ethylene. After being stirred overnight, the reaction mixture was quenched with ~15 mL of a solution of concentrated HCl in methanol (10:90 volume percent solution). The polymer was collected on a frit, washed with methanol and then acetone and then dried in vacuo overnight.

General Procedure for the Screening of Propylene Polymerization by Nickel Allyl Initiators at 48 kPa Propylene with Polymethylaluminoxane (PMAO) Cocatalyst.

In the drybox, the nickel complex was placed in a Schlenk flask and dissolved in ~ 10 mL of toluene. The flask was sealed, removed from the drybox and attached to an ethylene line where it was purged with first nitrogen and then propylene. After purging with propylene, PMAO was quickly added to the reaction mixture and the flask was placed under ~ 48 kPa of propylene. After being stirred overnight, the reaction mixture was quenched with ~ 10 mL of a solution of concentrated HCl in methanol (10:90 volume percent solution). The polymer was collected on a frit, washed

with methanol and then acetone and then dried in vacuo overnight.

General Procedure for the Screening of Propylene Polymerization by Nickel Allyl Initiators at 48 kPa Propylene with $B(C_6F_5)_3$ Cocatalyst.

In the drybox, the nickel complex was placed in a Schlenk flask and dissolved in ~10 mL of CH_2Cl_2. Two equiv of $B(C_6F_5)_3$ were dissolved in a minimal amount of CH_2Cl_2 and the solution was transferred to the Schlenk flask. The flask was sealed, removed from the drybox and attached to an ethylene line where it was purged with first nitrogen and then propylene. The flask was placed under ~48 kPa of propylene and the reaction mixture was stirred overnight and then was quenched with ~10 mL of a solution of concentrated HCl in methanol (10:90 volume percent solution). The polymer was collected on a frit, washed with methanol and then acetone and then dried in vacuo overnight

General Procedure for the Screening of Propylene Polymerization by Nickel Allyl Initiators at 600 kPa Propylene with $B(C_6F_5)_3$ Cocatalyst.

In the drybox, the nickel complex was placed in a vessel and dissolved in ~20 mL of CH_2Cl_2. Two equiv of $B(C_6F_5)_3$ were dissolved in 10 mL of CH_2Cl_2 and placed in a separate vessel. Both vessels were sealed and removed from the drybox. The solution of the nickel complex was transferred to a 100 mL Parr reactor under vacuum and the solution of $B(C_6F_5)_3$ was transferred to the addition port of the same reactor. The $B(C_6F_5)_3$ solution was forced into the reactor ~600 kPa of propylene. The reactor pressure was maintained at 600 kPa and the reaction mixture was stirred for 3 h. Next, the reaction mixture was quenched with ~ 10 mL of a solution of concentrated HCl in methanol (10:90 volume percent solution). If polymer was present, it was collected on a frit, washed with methanol and then acetone and then dried in vacuo overnight. Oligomers were characterized by GC analysis.

Table 1

Reaction Conditions Used in Ethylene and Propylene Polymerizations[a]

A	5 mL C_6D_6, rt, 18 h, 6.9 MPa E, 2 equiv BPh_3
B	5 mL $CDCl_3$, 80 °C, 18 h, 6.9 MPa E, 1 equiv $B(C_6F_5)_3$
C	5 mL C_6D_6, 80 °C, 18 h, 6.9 MPa E, 2 equiv BPh_3
D	5 mL C_6D_6, rt, 18 h, 6.9 MPa E, 1 equiv $B(C_6F_5)_3$
E	5 mL C_6D_6, 80 °C, 18 h, 6.9 MPa E, 2 equiv $B[3,5\text{-}C_6H_3\text{-}(CF_3)_2]_3$
F	5 mL $CDCl_3$, rt, 18 h, 6.9 MPa E, 2 equiv $B[3,5\text{-}C_6H_3\text{-}(CF_3)_2]_3$
G	5 mL $CDCl_3$, rt, 18 h, 6.9 MPa E, 2 equiv $B(C_6F_5)_3$
H	5 mL $CDCl_3$, 80 °C, 18 h, 6.9 MPa E, 2 equiv $B(C_6F_5)_3$
I	20 mL toluene, rt, overnight, 28-35 kPa E, excess PMAO
J	10 mL toluene, rt, overnight, 48 kPa P, excess PMAO
K	10 mL CH_2Cl_2, rt, overnight, 48 kPa P, 2 equiv $B(C_6F_5)_3$
L	30 mL CH_2Cl_2, rt, 3 h, 600 kPa P, 2 equiv $B(C_6F_5)_3$

[a]Abbreviations. E: Ethylene; P: Propylene; PMAO: Polymethylaluminoxane.

Table 2

Polymerization of Ethylene by Compounds 1-20 at 6.9 MPa Ethylene

Conditions A (5 mL C_6D_6, rt, 18 h, 2 equiv BPh_3)				Conditions B (5 mL $CDCl_3$, 80 °C, 18 h, 1 equiv $B(C_6F_5)_3$)			
Ex.	Cmpd[b]	PE (g)[c]	TO[d]	Ex.	Cmpd[b]	PE (g)[c]	TO[d]
41	**1a**	0.43[e]	260	61	**1a**	0.40[f]	240
42	**2a**	*a*	*a*	62	**2a**	1.2	730
43	**3a**	4.1	2400	63	**3a**	*a*	*a*
44	**4a**	12.7	7500	64	**4a**	*a*	*a*
45	**5a**	5.1	3000	65	**5a**	*a*	*a*
46	**6a**	1.3[g]	590	66	**6a**	1.09	650
47	**7a**	*a*	*a*	67	**7a**	0.14	81
48	**8a**	0.29	170	68	**8a**	2.65	1600
49	**9a**	0.70	410	69	**9a**	2.5	1500
50	**10a**	0.33	200	70	**10a**	*a*	*a*
51	**11a**	*a*	*a*	71	**11a**	0.24	140
52	**12a**	0.15	87	72	**12a**	0.16	95
53	**13a**	*a*	*a*	73	**13a**	0.66	390
54	**14a**	1.1	640	74	**14a**	1.2	730
55	**15a**	0.14	80	75	**15a**	0.21	120
56	**16a**	*a*	*a*	76	**16a**	2.3	1400
57	**17a**	0.52	310	77	**17a**	1.33	780
58	**18a**	0.35	590	78	**18a**	*a*	*a*
59	**19a**	0.53	310	79	**19a**	*a*	*a*
60	**20a**	0.14	81	80	**20a**	*a*	*a*

[a]Less that 0.1 g of polyethylene was isolated. [b]0.06 mmol [c]PE: Polyethylene. [d]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). [e]1 equiv of $B(C_6F_5)_3$ was used (Conditions D in Table 1). [f]5 mL C_6D_6 and 2 equiv BPh_3 were used (Conditions C in Table 1). [g]1 equiv BPh_3 was used.

Table 3
Characterization of Polyethylenes Produced by Complexes 1-20

Ex.	Cmpd (Conds)	Mw	Mn	PDI	Tm (°C)	NMR Analysis (Branching per 1000 CH_2)
81	1a(C)	703000	6640	106		^{1}H NMR: 16.5 Total Methyls
82	1a(D)	1320000	16100	81.6		^{13}C NMR: 74.0 Total Methyls; Branch Lengths: Methyl (38.7), Ethyl (11.0), Propyl (5.3), Butyl (5.9), Amyl (3), $\geq$Hex^{b} (4.5), $\geq$Am^{b} (11.3), $\geq$Bu^{b} (21.4)
83	1a(E)	259000	6550	39.5	68^{c} 110	^{1}H NMR: 54.9 Total Methyls
84	2a(B)	21100	2840	7.44	101	^{13}C NMR: 58.4 Total Methyls; Branch Lengths: Methyl (37.5), Ethyl (4.3), Propyl (2.3), Butyl (2), Amyl (2.4), $\geq$Hex^{b} (9.9), $\geq$Am^{b} (11.8), $\geq$Bu^{b} (14.4)
85	3a(A)				120	^{13}C NMR: 27.9 Total Methyls; Branch Lengths: Methyl (21.7), Ethyl (2.4), Propyl (0.5), Butyl (0.7), Amyl (0.4), $\geq$Hex^{b} (2.6), $\geq$Am^{b} (2.5), $\geq$Bu^{b} (3.3)
86	4a(A)					^{13}C NMR: 52.0 Total Methyls; Branch Lengths: Methyl (38.0), Ethyl (2.3), Propyl (2.5), Butyl (2.9), Amyl (2.5), $\geq$Hex^{b} (3.0), $\geq$Am^{b} (6.0), $\geq$Bu^{b} (5.4)
87	5a(A)	88600	11100	7.95		^{13}C NMR: 94.7 Total Methyls; Branch Lengths: Methyl (66.7), Ethyl (12.5), Propyl (0.5), Butyl (3.0), Amyl (3.3), $\geq$Hex^{b} (6.0), $\geq$Am^{b} (10.0), $\geq$Bu^{b} (9.8)
88	6a(A)	d	d	d		^{13}C NMR: 6.4 Total Methyls; Branch Lengths: Methyl (5.5)
89	6a(C-1)	19,600	7580	2.58		^{1}H NMR: 30.2 Total Methyls
90	6a(C-2)	12,700	3680	3.45	108	^{13}C NMR: 38.8 Total Methyls; Branch Lengths: Methyl (23.1), Ethyl (4.0), Propyl (1.8), Butyl (0), Amyl (0.9), $\geq$Hex^{b} (2.6), $\geq$Am^{b} (5.7), $\geq$Bu^{b} (9.6)

Table 3 (cont'd)

Characterization of Polyethylenes Produced by Complexes 1-20

Ex.	Cmpd (Conds)	Mw	Mn	PDI	Tm (^{o}C)	NMR Analysis (Branching per 1000 CH_2)
91	**6a(E)**	10800	2910	3.71	101	^{1}H NMR: 42.8 Total Methyls
92	**6a(F)**	128000	9040	14.1	131	^{1}H NMR: 3.1 Total Methyls
93	**7a(B)**	22300	6170	3.62	127	
94	**8a(A)**	d	d	d	130	
95	**8a(B)**	8770	1600	5.47	80	^{13}C NMR: 68.0 Total Methyls; Branch Lengths: Methyl (41.1), Ethyl (8.8), Propyl (0.5), Butyl (2.6), Amyl (5.6),$\geq$Hex^{b} (9.9),$\geq$Am^{b} (14.7),$\geq$Bu^{b} (16.8)
96	**9a(A)**	d	d	d	130	^{13}C NMR: 18.7 Total Methyls; Branch Lengths: Methyl (16.0)
97	**9a(B)**	60800	590	103	124	^{13}C NMR: 119.0 Total Methyls; Branch Lengths: Methyl (66.0),Ethyl (22.5), Propyl (5.0),Butyl (8.7),Amyl (7.5),$\geq$Hex^{b} (15.5),$\geq$Am^{b} (23.9),$\geq$Bu^{b} (28.4)
98	**10a(A)**	25600	6180	4.14	128	^{1}H NMR: 11.4 Total Methyls
99	**11a(B)**	77500	3090	25.1	119	
100	**13a(B)**	15500	3580	4.33	97	
101	**14a(A)**	d	d	d	129	
102	**14a(B)**	68900	3070	22.4	78	
103	**15a(B)**	23800	7560	3.15	129	^{1}H NMR: 57.8 Total Methyls

Table 3 (cont'd)

Characterization of Polyethylenes Produced by Complexes **1-20**

Ex.	Cmpd (Conds)	Mw	Mn	PDI	Tm (°C)	NMR Analysis (Branching per 1000 CH_2)
104	**16a(B)**	69400	885	78.4	117	^{13}C NMR: 48 Total Methyls; Branch Lengths: Methyl (24.8), Ethyl (5.9), Propyl (1), Butyl (2.6), Amyl (6), $\geq$Hex[b] (11.8), $\geq$Am[b] (14.2), $\geq$Bu[b] (16.3)
105	**17a(A)**	d	d	d	132	^{1}H NMR: 19.5 Total Methyls
106	**17a(B)**	325000	2080	156	128	^{13}C NMR: 25.2 Total Methyls; Branch Lengths: Methyl (17.9), Ethyl (4.3), Propyl (1.3), Butyl (1.9), Amyl (2.5), $\geq$Hex[b] (3.7), $\geq$Am[b] (4.4), $\geq$Bu[b] (0.8)
107	**18a(A)**	24800	8730	2.84		^{1}H NMR: 22.8 Total Methyls
108	**19a(A)**	90600	1630	55.7	123	^{13}C NMR: 47.4 Total Methyls; Branch Lengths: Methyl (23.7), Ethyl (5.6), Propyl (1.4),Butyl (2.1),Amyl (6.6),$\geq$Hex[b] (12.7),$\geq$Am[b] (14.8),$\geq$Bu[b] (16.7)

[a]Reaction conditions are given in Table 1. [b]Includes ends of chains. [c]Heterogeneous conditions in the glass insert during mixing can account for the observation of two Tm's. [d]GPC could not be performed due to the insolubility of the sample.

Table 4

Polyethylene Yields: Demonstration of Effects of Reaction Conditions and Reproducibility of Yields Using Rapid Screening Techniques with Compound 6

		Polyethylene Yield (g)				
Ex.	Reaction Conditions[b]	Run 1	Run 2	Run 3	Run 4	Run 5
109 - 113	A: 5 mL C_6D_6, rt, 18 h, 6.9 MPa E, 2 equiv BPh_3	a	0.10	0.10	a	1.3[c]
114 - 115	B: 5 mL $CDCl_3$, 80 °C, 18 h, 6.9 MPa E, 1 equiv $B(C_6F_5)_3$	0.10	0.28			
116 - 118	C: 5 mL C_6D_6, 80 °C, 18 h, 6.9 MPa E, 2 equiv BPh_3	9.50	9.55	0.49[d]		
119 - 121	G: 5 mL $CDCl_3$, rt, 18 h, 6.9 MPa E, 2 equiv $B(C_6F_5)_3$	a	0.65	7.78		
122 - 123	H: 5 mL $CDCl_3$, 80 °C, 18 h, 6.9 MPa E, 2 equiv $B(C_6F_5)_3$	1.09	1.09			

[a]Less than 0.1 g of polyethylene was isolated. [b]E: Ethylene; $H^2(CO_2Me)CH_2$ initiator was used unless otherwise noted. [c]1 equiv of BPh_3 was used. [d]$H_2CCHCHCl$ allyl initiator was used.

Table 5

Polymerization of Ethylene and Propylene at Low Pressures

Ex.	Cmpd (mmol)	Conds[a]	Gas (kPa)[b]	Polymer (g)	TO[c]	T_m (°C)
124	**1a** (0.11)	I	E (27-35)	2.91	970	d
125	**6a** (0.12)	I	E (27-35)	0.42	128	125
126	**15a** (0.15)	I	E (27-35)	0.11	27	121[e]
127	**20a** (0.11)	I	E (27-35)	0.27	88	f
128	**1a** (0.06)	J	P (48)	1.84	730	g
129	**1a** (0.06)	K	P (48)	0.21	81	h
130	**6a** (0.06)	L	P (600)	11.2[i]	4400[i]	j

[a]Reaction conditions are defined in Table 1. [b]E: Ethylene. P: Propylene. [c]TO: number of turnovers per catalyst center = (moles monomer consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). [d]Clear, rubbery amorphous PE. [e]White, rubbery PE. [f]White, crystalline PE. [g]Clear rubbery PP. [h]Clear sticky PP. [i]14 mL of liquid oligomers were isolated. A density of 0.8 g/mL was assumed. [j]GC analysis indicates that pentamers, hexamers and heptamers predominate.

Examples 131-136

Styrene and Norbornene Homo- and Copolymerizations

In the subsequent examples describing polymerizations of styrene and norbornene, all manipulations were carried out in a nitrogen-purged drybox. Anhydrous solvents were used. The styrene (99+%, Aldrich, inhibited with 4-*tert*-butylcatechol) was degassed, filtered through basic alumina and inhibited with phenothiazine (98+%, Aldrich, 50 ppm) before use. The norbornene was purified by vacuum sublimation. Tacticities of polystyrenes were measured according to the following reference: T Kawamura et al., *Macromol. Rapid Commun.* **1994**, *15,* 479-486.

General Procedure for Styrene Polymerizations. The nickel complex (0.03 mmol) was slurried in dry toluene (6 mL) and styrene (1.3 mL, 1.18 g, 11.3 mmol) was added. Two equiv of $B(C_6F_5)_3$ were then added with vigorous stirring. The resulting mixture was shaken at rt in the dark for 16 h after which time the sample was removed from the drybox and MeOH was added to precipitate the polymer. The solid polymer was isolated, redissolved in $CHCl_3$ and reprecipitated with MeOH to remove catalyst impurities. The product was then collected on a frit, washed with MeOH and finally with a MeOH/acetone/Irganox® 1010 solution.

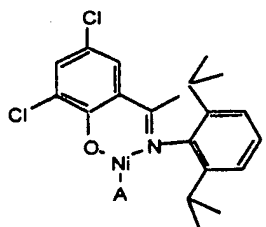
General Procedure for Norbornene Polymerizations. The nickel complex (0.03 mmol) was slurried in dry toluene (6 mL) and norbornene (1.6 g, 17.0 mmol) was added. Two equiv of $B(C_6F_5)_3$ were then added with vigorous stirring. The resulting mixture was shaken at rt. After 16 h, the sample was removed from the drybox and MeOH was added to precipitate the polymer. The solid polymer was isolated. The polymer was redissolved or swollen with solvent in order to remove catalyst impurities and then reprecipitated with MeOH. The product was then collected on a frit, washed with MeOH and finally with an acetone/2% Irganox® 1010 solution.

General Procedure for Styrene/Norbornene Copolymerizations. The nickel complex (0.03 mmol) was slurried in dry toluene (5 mL) and a mixture of norbornene (1.17 g, 12.4 mmol) and styrene (1.4 mL, 1.27 g, 12.2 mmol) in toluene (3 mL) was added. Two equiv of $B(C_6F_5)_3$ were then added with vigorous stirring. The resulting mixture was shaken at rt in the dark for 5 h. The sample was then removed from the drybox and MeOH was added to precipitate the polymer. The isolated polymer was dissolved ($CHCl_3$) and reprecipitated (MeOH) to remove the catalyst residue. The product was stirred overnight in acetone to remove polystyrene and then filtered, washed with MeOH and finally with an acetone/2% Irganox® 1010 solution.

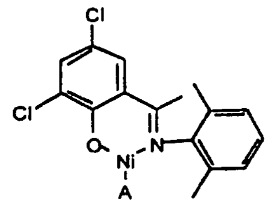
Table 6
Styrene (S) and Norbornene (N) Homo- and Copolymerizations

Ex.	Cmpd	Monomers	Yield (%)	TO[a] S	TO[a] N	Mn[b]	PDI	% S
131	**3a**	S	79	300	-	2140	1.9	100[c]
132	**6a**	S	54	200	-	3390	1.8	100[c]
133	**3a**	N	>95	-	570	*d*	*d*	Ñ
134	**6a**	N	>95	-	570	*d*	*d*	Ñ
135	**3a**	S, N	21	13	170	9580	2.5	8
136	**6a**	S, N	7	4	56	15500	2.0	7

[a]Number of turnovers: TO = (moles monomer consumed, as determined by the weight of the isolated polymer) divided by (moles catalyst). [b]M_n (GPC, TCB 120°C, polystyrene standards). [c]^{13}C NMR spectroscopy ($CDCl_3$) indicates enrichment in meso diad units relative to atactic polystyrene. [d]Within 30 min the reaction mixture completely solidified and attempts to redissolve the polymer were unsuccessful. The insolubility of the polymer product indicates that an addition polymer of norbornene was formed.



21



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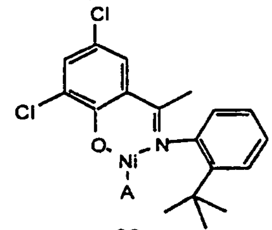

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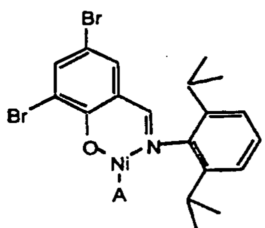

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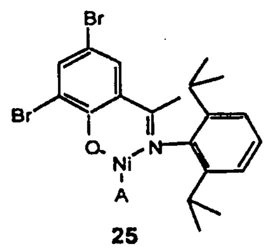

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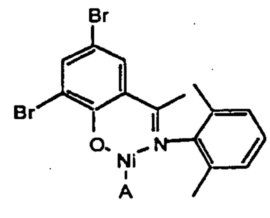

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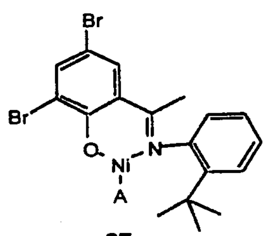

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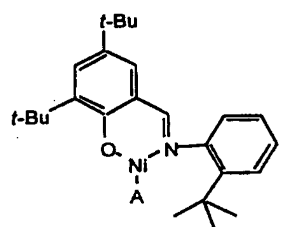

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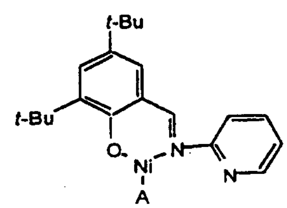

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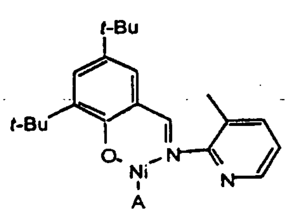

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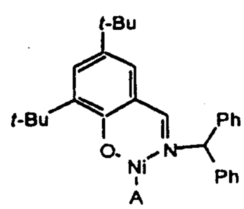

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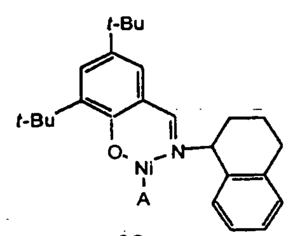

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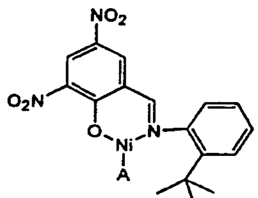

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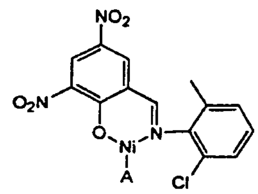

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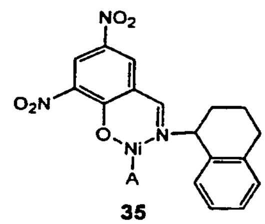

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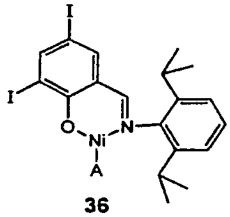

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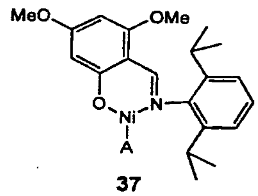

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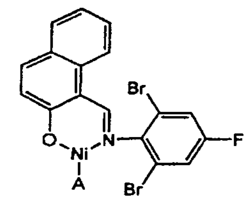

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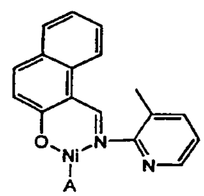

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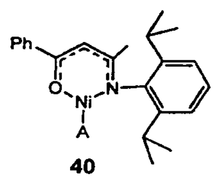

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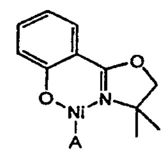

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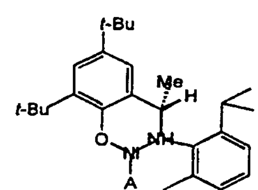

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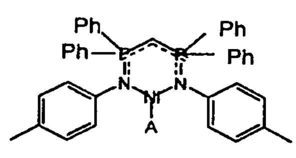

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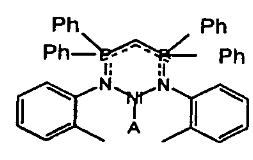

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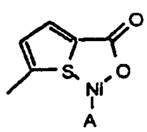

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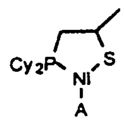

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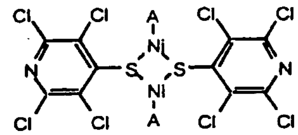

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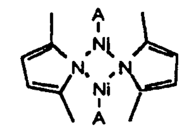

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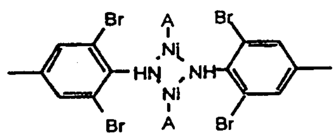

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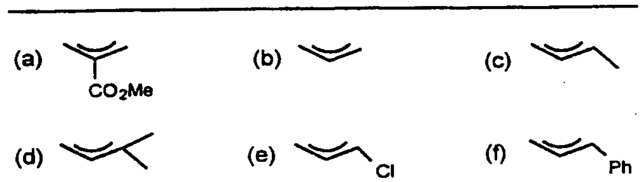
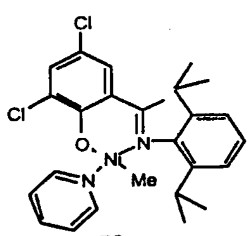
A (Allyl)





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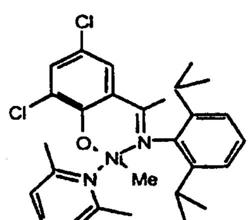

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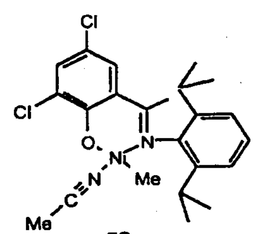

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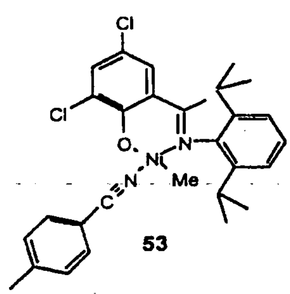

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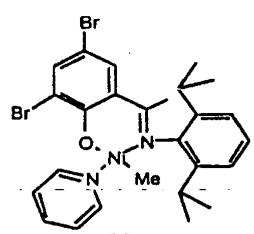


54

Compounds **21-54**. The syntheses and characterization of compounds **21-60** and their ligand precursors are reported in Examples 467 to 498. These compounds are used in the following Examples.

Examples 137 - 187

Styrene Homopolymerizations and Styrene/Norbornene Copolymerizations

In the subsequent examples describing polymerizations of styrene and norbornene, all manipulations were carried out in a nitrogen-purged drybox. Anhydrous solvents were used. The styrene (99+%, Aldrich, inhibited with 4-*tert*-butylcatechol) was degassed, filtered through basic alumina and inhibited with phenothiazine (98+%, Aldrich, 50 ppm) before use. The norbornene was purified by vacuum sublimation. Tacticities of polystyrenes were measured according to the following reference: T Kawamura et al., *Macromol. Rapid Commun.* **1994**, *15,* 479-486.

General Procedure for Styrene Polymerizations (Table 7). The nickel complex (0.03 mmol) was slurried in dry toluene (6 mL) and styrene (1.6 mL, 14 mmol) was added. Two equiv of $B(C_6F_5)_3$ were then added with vigorous stirring. The resulting mixture was shaken at rt in the dark for 5 h after which time the sample was removed from the drybox and MeOH was added to precipitate the polymer. The solid polymer was isolated, redissolved in $CHCl_3$ and reprecipitated with MeOH to remove catalyst impurities. The product was then collected on a frit, washed with MeOH and finally with a MeOH/ acetone/Irganox® 1010 solution. The polymer was then dried under vacuum.

General Procedure for Styrene/Norbornene Copolymerizations (Table 8). The nickel complex (0.03 mmol) was slurried in dry toluene (5 mL) and a mixture of norbornene (1.41 g, 15 mmol) and styrene (1.7 mL, 15 mmol) in toluene (3 mL) was added. Two equiv of $B(C_6F_5)_3$ were then added with vigorous stirring. The resulting mixture was shaken at rt in the dark overnight. The sample was then removed from the drybox and added to MeOH to precipitate the polymer. The product was stirred overnight in acetone to remove polystyrene and then filtered, washed with MeOH and

finally with an acetone/2% Irganox 1010 solution. The polymer was then dried under vacuum.

Table 7
Styrene Homopolymerizations

Ex.	Cmpd	Yield (%)	TO[a]	M_n[b]	PDI	Tacticity
137	**1a**	e	e			
138	**2a**	e	e			
139	**4a**	41	192	16,000	2.0	enriched in meso diads[c]
140	**5a**	61	282	14,900	2.1	enriched in meso diads[c]
141	**8a**	15	70	2,390	3.8	enriched in meso diads[c]
142	**9a**	0.7	3.2			
143	**14a**	36	170	2,010	5.4	enriched in meso diads[c]
144	**15a**	31	144	1,350	2.4	enriched in meso diads[c]
145	**16a**	e	e			
146	**17a**	9	42	5,800	2.2	enriched in meso diads[c]
147	**21a**	72	336	770	2.7	enriched in meso diads[c]
148	**22a**	66	304	760	2.7	enriched in meso diads[c]
149	**24a**	73	340	1,010	2.9	enriched in meso diads[c]
150	**28a**	48	221	730	2.9	enriched in meso diads[c]
151	**31a**	57	265	2,230	1.8	enriched in meso diads[c]
152	**32a**	78	362	14,900	2.1	enriched in meso diads[c]
153	**33a**	26	122	830	2.3	enriched in meso diads[c]
154	**35a**	6	29	18,800	5.1	highly isotactic
155	**35a**[d]	29	134	4,150	6.8	highly isotactic
156	**39a**	4.1	19			enriched in r diads[c]
157	**40a**	58	269	785	3.5	enriched in meso diads[c]
158	**42a**	57	265	800	2.8	enriched in meso diads[c]
159	**46a**	6	29	1,980	1.4	highly isotactic
160	**47b**	15	70	1,200	6.3	enriched in meso diads[c]
161	**48a**	48	221	1,660	8.3	enriched in meso diads[c]
162	**49a**	9	42	12,200	2.6	enriched in meso diads[c]

[a]Number of turnovers: TO = (moles styrene consumed, as determined by the weight of the isolated polymer) divided by (moles catalyst). [b]M_n (GPC, TCB, 120°C, polystyrene standards). [c]According to ^{13}C NMR spectroscopy ($CDCl_3$) and relative to atactic polystyrene. [d]60 °C. [e]No polymer was isolated.

Table 8
Styrene (S) and Norbornene (N) Copolymerizations

			TO[a]				
Ex.	Cmpd	Yield (%)	S	N	M_n[b]	PDI	% S
163	**1a**	4.7	c	47	5,330	5	<5
164	**2a**	40	c	400	11,000	3.9	<5
165	**4a**	43	44	390	7,630	3.3	11
166	**5a**	27	15	251	5,430	2.3	6.7
167	**8a**	14	c	141	14,300	2.7	<5
168	**9a**	8.5	c	84	8,100	2.3	<5
169	**14a**	32	17	303	7,290	3.4	5.8
170	**15a**	36	29	329	7,140	3.0	9
171	**16a**	8.8	c	92	6,920	2.6	<5
172	**17a**	7.8	c	78	7,060	2.3	<5
173	**21a**	44	41	400	2,730	3.8	10.2
174	**22a**	47	45	425	3,340	3.3	10.5
175	**24a**	15	5	142	5,800	3.0	3.7
176	**28a**	45	47	415	2,680	3.9	11.2
177	**31a**	30	c	300	4,700	2.4	<5
178	**32a**	26	19	236	5,670	2.2	7.5
179	**33a**	31	13	300	5,940	2.6	4.5
180	**35a**	7.4	c	74	20,500	2.4	<5
181	**39a**	3.0	c	262	5,054	2.9	<5
182	**40a**	18	5	172	5,960	2.9	3.0
183	**42a**	43	31	398	2,470	4.4	8.7
184	**46a**	38	c	379	14,800	2.8	<5
185	**47b**	17	c	170	4,570	6.2	<5
186	**48a**	8	c	78	17,600	2.5	<5
187	**49a**	15	c	145	7,500	2.3	<5

[a]Number of turnovers: TO = (moles monomer consumed, as determined by the weight of the isolated polymer) divided by (moles catalyst). [b]M_n (GPC, TCB, 120°C, polystyrene standards). [c]Low styrene incorporation (<5%) precluded calculation of the styrene turnover numbers.

Examples 188 - 194

Norbornene Homopolymerizations and Norbornene/Functionalized-Norbornene Copolymerizations

Example 188

Norbornene Homopolymerization Catalyzed by **52**/$B(C_6F_5)_3$.

In a 20 mL scintillation vial under nitrogen, compound **52** (0.010 g, 0.021 mmol) and norbornene (1.00 g, 10.62 mmol) were dissolved in 5 mL of toluene to give an orange solution. To this was added $B(C_6F_5)_3$ (0.011 g, 0.022 mmol). After 30 min at ambient temperature, more $B(C_6F_5)_3$ was added to the reaction mixture (0.110 g, 0.214 mmol). An extremely viscous, yellow suspension formed very rapidly and within minutes the reaction mixture could no longer be stirred. Twenty-three h after the initial addition of $B(C_6F_5)_3$, the reaction mixture was quenched by addition of methanol under air. Further workup afforded 0.93 g of polymer. ^1H NMR (1,1,2,2-tetrachloroethane-d_2, 120°C) indicated that the polymer was the addition polymer of norbornene formed without double bond ring-opening.

Example 189

Copolymerization of Norbornene with the Dimethyl Ester of endo-5-Norbornene-2,3-Dicarboxylic Acid Catalyzed by **21a**/$B(C_6F_5)_3$ (Copolymer: ~30 Mole % Dimethyl Ester)

In a 20 mL scintillation vial under nitrogen, compound **21a** (0.015 g, 0.029 mmol), norbornene (0.500 g, 5.31 mmol), and the dimethyl ester of 5-norbornene-2,3-dicarboxylic acid (1.00 g, 4.76 mmol) were dissolved in 10 mL of toluene. To this solution was added solid $B(C_6F_5)_3$ (0.029 g, 0.058 mmol). The resulting solution was stirred initially at ambient temperature by means of a magnetic stirbar; however, after several minutes the reaction mixture consisted of a viscous, solvent-swollen polymer that could not be stirred. Twenty-seven h after the addition of $B(C_6F_5)_3$, the reaction mixture was quenched by addition of the solvent-swollen reaction mixture to methanol under air. The precipitated polymer was filtered off, washed with methanol, and dried to afford 0.810 g of addition copolymer. ^1H NMR (CD_2Cl_2, 25 °C) indicated the

following composition: norbornene (74 mole %), dimethyl ester (26 mole %). Quantitative ^{13}C NMR (trichlorobenzene-d_3, 100 °C) indicated the following composition: norbornene (70.8 mole %), dimethyl ester (29.2 mole %).

Example 190

Copolymerization of Norbornene with the Dimethyl Ester of endo-5-Norbornene-2,3-Dicarboxylic Acid Catalyzed by **21a**/$B(C_6F_5)_3$ (Copolymer: ~22 Mole % Dimethyl Ester)

A reaction identical to that above in Example 189, but run in CH_2Cl_2 instead of toluene gave the following results: Yield = 0.63 g. ^1H NMR ($CDCl_3$, 25 °C) indicated the following composition: norbornene (81%), dimethyl ester (19%). Quantitative ^{13}C NMR (trichlorobenzene-d_3, 100 °C): norbornene (78.11 mole %), dimethyl ester (21.89 mole %).

Example 191

Copolymerization of Norbornene with the Dimethyl Ester of endo-5-Norbornene-2,3-Dicarboxylic Acid Catalyzed by **21a**/$B(C_6F_5)_3$ (Copolymer: ~11 mole % Dimethyl Ester)

In a 20 mL scintillation vial under nitrogen, compound **21a** (0.015 g, 0.029 mmol), norbornene (3.00 g, 31.86 mmol), the dimethyl ester of 5-norbornene-2,3-dicarboxylic acid (1.00 g, 4.76 mmol), and $B(C_6F_5)_3$ (0.029 g, 0.058 mmol) were dissolved in 10 mL of toluene. The resulting yellow solution was stirred initially at ambient temperature by means of a magnetic stirbar; however, within 15 minutes an extremely rapid, highly exothermic reaction ensued. The reaction mixture setup and could not be stirred after this point. Three h after the addition of $B(C_6F_5)_3$, the reaction mixture was quenched by addition of the solvent-swollen reaction mixture to methanol under air. Further workup afforded 3.75 g of addition copolymer. ^1H NMR ($CDCl_3$, 25 °C) indicated the following composition: norbornene (90 mole %), dimethyl ester (10 mole %). Quantitative ^{13}C NMR (trichlorobenzene-d_3,

100 °C) indicated the following composition: norbornene (89.05 mole%), dimethyl ester (10.95 mole%).

Example 192

Copolymerization of Norbornene with the Dimethyl Ester of endo-5-Norbornene-2,3-Dicarboxylic Acid Catalyzed by **21a** / $B(C_6F_5)_3$ (Copolymer: ~6 mole % Dimethyl Ester)

A reaction identical to that above in Example 191, but run in CH_2Cl_2 instead of toluene gave the following results: Yield = 3.12 g. ^1H NMR ($CDCl_3$, 25 °C) indicated the following composition: norbornene (96 mole %), dimethyl ester (4 mole %). Quantitative ^{13}C NMR (trichlorobenzene-d_3, 100 °C): norbornene (94.19 mole %), dimethyl ester (5.81 mole %).

Example 193

Copolymerization of Norbornene with the t-Bu Ester of 5-Norbornene-2-Carboxylic Acid Catalyzed by **50**/$B(C_6F_5)_3$ (Copolymer: ~30 mole % t-Bu Ester)

In a 20 mL scintillation vial under nitrogen, compound **50** (0.010 g, 0.020 mmol), norbornene (0.500 g, 5.31 mmol), and the t-Bu ester of 5-norbornene-2-carboxylic acid (1.00 g, 5.15 mmol) were dissolved in 5 mL toluene. To this solution was added $B(C_6F_5)_3$ (0.102 g, 0.200 mmol). The resulting yellow solution was stirred at ambient temperature for 16 h. The reaction mixture was quenched and the copolymer precipitated by addition of methanol under air. Further workup afforded 0.664 g of addition copolymer. Quantitative ^{13}C NMR (trichlorobenzene-d_3, 100 °C) indicated the following composition: norbornene (70.4 mole %), t-Bu ester (29.6 mole %).

Example 194

Copolymerization of Norbornene with the Dimethyl Ester of endo-5-Norbornene-2,3-Dicarboxylic Acid Catalyzed by **52**/$B(C_6F_5)_3$ (Copolymer: ~32 mole % Dimethyl Ester)

In a 20 mL scintillation vial under nitrogen, compound **52** (0.010 g, 0.021 mmol), norbornene (0.500 g, 5.31 mmol), and the dimethyl ester of 5-norbornene-2,3-dicarboxylic acid (1.00 g, 4.76 mmol) were dissolved in

5 mL of toluene. To this solution was added a suspension of $B(C_6F_5)_3$ (0.029 g, 0.058 mmol) in 5 mL of toluene. The resulting orange solution was stirred initially at ambient temperature by means of a magnetic stirbar; however, after several minutes the reaction mixture consisted of a viscous, solvent-swollen polymer that could not be stirred. Twenty-two h after the addition of $B(C_6F_5)_3$, the reaction mixture was quenched by addition of the solvent-swollen reaction mixture to methanol under air. The precipitated polymer was filtered off, washed with methanol, and dried to afford 0.930 g of addition copolymer. ^1H NMR ($CDCl_3$, 25 °C) indicated the following composition: norbornene (68 mole %), dimethyl ester (32 mole %).

Examples 195 - 366

Ethylene Polymerizations

General Procedure for Ethylene Polymerizations of Table 9

Pressure Tube Loaded Outside of the Drybox Under a Nitrogen Purge

(In the ethylene polymerization reactions of Tables 2, 3, and 4, the glass inserts were also loaded in the pressure reactor tube outside of the drybox under a nitrogen purge.) Procedure. In the drybox, a glass insert was loaded with the isolated allyl initiator (0.06 mmol). The insert was cooled to -35°C in the drybox freezer, 5 mL of C_6D_6 was added to the cold insert, and the insert was cooled again. A Lewis acid cocatalyst [typically BPh_3 or $B(C_6F_5)_3$] was added to the cold solution, and the insert was then capped and sealed. Outside of the drybox, the cold insert was placed under a nitrogen purge into the pressure tube. The pressure tube was sealed, placed under ethylene (6.9 MPa), and allowed to warm to rt as it was shaken mechanically for approximately 18 h. An aliquot of the solution was used to acquire a ^1H NMR spectrum. The remaining portion was added to ~20 mL of MeOH in order

to precipitate the polymer. The polyethylene was isolated and dried under vacuum.

General Procedure for Ethylene Polymerizations of Tables 10-14:

Pressure Tube Loaded and Sealed in the Drybox under a Nitrogen Atmosphere

Procedure. In the drybox, a glass insert was loaded with the nickel compound. Often, a Lewis acid (typically BPh_3 or $B(C_6F_5)_3$) was also added to the glass insert. Next, 5 mL of a solvent (typically 1,2,4-trichlorobenzene although *p*-xylene, cyclohexane, etc. were also used at times) was added to the glass insert and the insert was capped. The glass insert was then loaded in the pressure tube inside the drybox. The pressure tube containing the glass insert was then sealed inside of the drybox, brought outside of the drybox, connected to the pressure reactor, placed under the desired ethylene pressure and shaken mechanically. After the stated reaction time, the ethylene pressure was released and the glass insert was removed from the pressure tube. The polymer was precipitated by the addition of MeOH (~20 mL) and concentrated HCl (~1-3 mL). The polymer was then collected on a frit and rinsed with HCl, MeOH, and acetone. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. The polymer yield and characterization were then obtained.

Table 9
Ethylene Polymerization (6.9 MPa, C_6D_6 (5 mL), 0.06 mmol Cmpd, 18 h)

Ex.	Cmpd	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^{1}H NMR)	Total Me[d]
195	**21a**	25	BPh_3	3.34	2,000	MI: 79.5; M_n(^{1}H): 3,670	36.9
196	**21a**	80	$B(C_6F_5)_3$	e	e		
197	**22a**	25	BPh_3	4.41	2,600	MI > 200; M_n(^{1}H): 1,890	85.5
198	**22a**	80	$B(C_6F_5)_3$	0.04	20		
199	**24a**	25	BPh_3	15.3	9,100	MI<0.01;M_n(^{1}H):no olefins	4.5
200	**24a**	80	$B(C_6F_5)_3$	0.15	91		
201	**28a**	25	BPh_3	0.30	180	M_n(^{1}H): 18,900	67.1
202	**28a**	80	$B(C_6F_5)_3$	0.04	24		
203	**31a**	25	BPh_3	f	f		
204	**31a**	80	$B(C_6F_5)_3$	f	f		
205	**32a**	25	BPh_3	0.01[e]	7[e]		
206	**32a**	80	$B(C_6F_5)_3$	e	e		
207	**33a**	25	BPh_3	0.21	120		
208	**33a**	80	$B(C_6F_5)_3$	1.60	950	MI: 79.5; M_n(^{1}H): 1,390	51.2
209	**35a**	25	BPh_3	0.19[e]	110[e]		
210	**35a**	80	$B(C_6F_5)_3$	0.11[e]	68[e]		
211	**37a**	25	BPh_3	0.02[e]	10[e]		
212	**38a**	80	$B(C_6F_5)_3$	0.07[e]	42[e]		
213	**39a**	25	BPh_3	f	f		
214	**39a**	80	$B(C_6F_5)_3$	2.11	1,300	MI: 105; M_n(^{1}H): 5,200	21.5
215	**40a**	25	BPh_3	0.08[e]	50[e]		
216	**40a**	80	$B(C_6F_5)_3$	e	e		
217	**42a**	25	BPh_3	e	e		
218	**42a**	80	$B(C_6F_5)_3$	e	e		

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at -806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [e]^{1}H NMR: oligomers and/or $(CH_2)_n$ peak observed. [f]PE was not obtained in isolable quantities.

Table 9 (Cont'd)

Ethylene Polymerization (6.9 MPa, C_6D_6 (5 mL), 0.06 mmol Cmpd, 18 h)

Ex.	Cmpd	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^1H NMR)	Total Me[d]
219	46a	25	BPh_3	f	f		
220	46a	80	$B(C_6F_5)_3$	0.11	65		
221	47b	25	BPh_3	0.12[e]	71[e]		
222	47b	80	$B(C_6F_5)_3$	e	e		
223	47b	25	BPh_3	0.15	91		
224	47b	80	$B(C_6F_5)_3$	0.09	52		
225	48a	25	BPh_3	0.07	43		
226	48a	80	$B(C_6F_5)_3$	0.22[e]	132[e]		
227	49a	25	BPh_3	0.10	59		
228	49a	80	$B(C_6F_5)_3$	0.06[e]	34[e]		

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at -806MS 4G 734/602005, RI detector), and/or ^1H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^1H NMR analysis. [e]^1H NMR: oligomers and/or $(CH_2)_n$ peak observed. [f]PE was not obtained in isolable quantities. [g]The general procedure for the screening of ethylene polymerizations by nickel allyl initiators at 6.9 MPa ethylene (*see above*) was followed.

Table 10

Ethylene Polymerizations at 6.9 MPa: Pressure Tube Loaded in the Drybox under N_2 Atmosphere (Trichlorobenzene (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^{1}H NMR)	Total Me[d]
229	3a	25	BPh_3	8.31	12,900	MI: 5.5; $M_n(^1H)$: 18,100	36.9
230	3a[g]	25	BPh_3	1.54	3,660	MI: 40; $M_n(^1H)$: no olefins	20.0
231	3a[g]	25	$B(C_6F_5)_3$	0.701	1,460	MI: 22.9; $M_n(^1H)$: 99,900	22.9
232	3a	80	BPh_3	4.29	6,640	MI > 200; $M_n(^1H)$: 4,770	56.2
233	3a	80	$B(C_6F_5)_3$	0.203	359	Mn (^{1}H): 2,500	47.7
234	4a	25	BPh_3	2.44	4,630	MI: 126; $M_n(^1H)$: 10,300	43.5
235	4a	80	BPh_3	2.19	3,640	MI > 200; $M_n(^1H)$: 2,270	75.5
236	4a	80	$B(C_6F_5)_3$	0.096	190	Mn (^{1}H): 3,260	29.3
237	5a	25	BPh_3	4.98	8,630	M_w(GPC): 14,100; PDI:6.7	93.2
238	5a	80	BPh_3	2.72	4,710	M_w(GPC): 2,850; PDI: 3.7	137.3
239	6a	25	BPh_3	4.44	7,730	MI: 0.85	
240	6a[i]	25	$B(C_6F_5)_3$	6.18	5,490	MI: 1.2; $M_n(^1H)$: 9,620	28.5
241	6a[g]	80	BPh_3	4.13	10,500	MI: 21; $M_n(^1H)$: 12,200	28.4
242	6a[h]	80	BPh_3	13.1	7,800	MI > 200; $M_n(^1H)$: 3,030	79.0
243	6a	80	$B(C_6F_5)_3$	3.31	5,990	MI: 81; $M_n(^1H)$: 5,920	34.7
244	6a[g]	80	$B(C_6F_5)_3$	3.14	7,300	MI: 45	
245	6a[h]	80	$B(C_6F_5)_3$	8.92	5,300	MI > 200; $M_n(^1H)$: 1,420	89.1
246	7a	25	BPh_3	0.93	1,350	MI<0.01;$M_n(^1H)$:no olefins	2.1
247	7a	25	$B(C_6F_5)_3$	2.19	3,790	$M_n(^1H)$: 4,160	11.6
248	7a	80	$B(C_6F_5)_3$	1.36	2,030	MI: 35; $M_n(^1H)$: 1,370	35.7
249	8a	25	BPh_3	3.88	6,400	MI: 120; $M_n(^1H)$: 2,990	57.2
250	8a	25	$B(C_6F_5)_3$	6.95	11,800	MI: 2.6; $M_n(^1H)$: 6,770	57.5
251	8a	80	$B(C_6F_5)_3$	3.99	7,220	MI: 132	

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol. [i]0.04 mmol.

Table 10 (Cont'd)
Ethylene Polymerizations at 6.9 MPa Pressure Tube Loaded in the Drybox under N_2 Atmosphere (Trichlorobenzene (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^{1}H NMR)	Total Me[d]
252	9a	25	BPh_3	6.35	11,200	MI > 200; $M_n(^1H)$: 4,910	64.9
253	9a	25	$B(C_6F_5)_3$	6.32	9,900	MI: 102; $M_n(^1H)$: 5,380	91.3
254	9a	80	$B(C_6F_5)_3$	4.8	8,000	$M_n(^1H)$: 1,410	134.6
255	10a	25	BPh_3	0.18	320		
256	10a	80	BPh_3	1.33	2,140	MI: 63; $M_n(^1H)$: 11,100	38.3
257	10a	80	$B(C_6F_5)_3$	0.097	170	$M_n(^1H)$: 2,010	30.4
258	11a	25	BPh_3	0.11	190		
259	11a	80	BPh_3	1.33	2,140	MI: 160; $M_n(^1H)$: 7,990	40.5
260	12a	25	BPh_3	3.68	6,040	MI < 0.01	
261	12a	80	BPh_3	4.22	7,260	MI: 74; $M_n(^1H)$: 9,260	33.0
262	12a	80	$B(C_6F_5)_3$	1.61	2,870	MI: 30; $M_n(^1H)$: 12,700	19.3
263	13a	25	BPh_3	0.99	1,690	MI: 0.04; $M_n(^1H)$: 23,400	20.5
264	13a	80	BPh_3	3.73	6,580	MI: 147; $M_n(^1H)$: 4,890	40.2
265	13a	80	$B(C_6F_5)_3$	0.93	1,560	MI > 200; $M_n(^1H)$: 4,520	36.5
266	14a	25	BPh_3	1.68	3,120	MI: 0.3; $M_n(^1H)$: 18,300	24.2
267	14a	25	$B(C_6F_5)_3$	4.28	7,010	MI: 6; $M_n(^1H)$: 5,820	42.6
268	14a	80	$B(C_6F_5)_3$	1.52	2,760	MI: 117; $M_n(^1H)$: 3,080	54.0
269	15a	25	BPh_3	0.265	468[e]		
270	15a	25	BPh_3	1.75	3,060	MI: 0.1; $M_n(^1H)$: 1,900	30.7
271	15a	80	$B(C_6F_5)_3$	0.399	705	$M_n(^1H)$: 1,700	43.7
272	17a	25	BPh_3	0.191	346	$M_n(^1H)$: 23,500	21.1
273	17a	25	$B(C_6F_5)_3$	5.69	10,100	MI < 0.01; $M_n(^1H)$: 24,600	10.4
274	17a	80	$B(C_6F_5)_3$	1.59	2,540	MI: 0.08; $M_n(^1H)$: 7,130	24.1

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190°C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol.

Table 10 (Cont'd)

Ethylene Polymerizations at 6.9 MPa Pressure Tube Loaded in the Drybox under N_2 Atmosphere (Trichlorobenzene (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^1H NMR)	Total Me[d]
275	18a	25	BPh_3	e	e		
276	18a	80	$B(C_6F_5)_3$	0.046	76	$M_n(^1H)$: 4,690	27.4
277	19a	25	BPh_3	0.289	544	$M_n(^1H)$: 4,450	36.2
278	19a	25	$B(C_6F_5)_3$	0.223	399	$M_n(^1H)$: 1,660	27.8
279	19a	80	BPh_3	0.077	128	$M_n(^1H)$: 2,550	39.3
280	19a	80	$B(C_6F_5)_3$	0.224	399	$M_n(^1H)$: 839	52.5
281	21a	25	BPh_3	6.48	10,700	MI: 42; $M_n(^1H)$: 21,400	24.9
282	21a	80	BPh_3	3.44	6,090	MI > 200; $M_n(^1H)$: 4,010	52.5
283	21a	80	$B(C_6F_5)_3$	0.123	226		
284	21b	25	BPh_3	4.15	6,060	MI: 16.5; $M_n(^1H)$: 21,600	19.9
285	21b	25	$B(C_6F_5)_3$	0.024	31	$M_n(^1H)$: 1,570	34.2
286	21b	80	BPh_3	3.39	5,640	MI > 200; $M_n(^1H)$: 3,730	55.2
287	21b	80	$B(C_6F_5)_3$	0.030	48	$M_n(^1H)$: 2,190	38.7
288	22a	25	BPh_3	10.1	17,900	MI > 200; $M_n(^1H)$: 2,600	85.1
289	22a	80	BPh_3	4.11	7,120	Mn (^1H): 1,630	92.6
290	22a	80	$B(C_6F_5)_3$	0.15	260	Mn (^1H): no olefins	23.7
291	23a	25	BPh_3	2.93	4,770	MI > 200; $M_n(^1H)$: 7,220	59.1
292	23a	25	BPh_3	2.90	4,960	MI: 120; $M_n(^1H)$: 8,950	56.5
293	23a	80	$B(C_6F_5)_3$	e	e		
294	24a	25	BPh_3	1.73	3,250	MI<0.01;$M_n(^1H)$:no olefins	8.6
295	24a	80	BPh_3	1.95	3,340	MI: 29; $M_n(^1H)$: 8,110	28.6
296	24a	80	$B(C_6F_5)_3$	1.16	2,060	MI: 70; $M_n(^1H)$: 8,540	23.0
297	25a	25	BPh_3	9.07	17,000	MI: 1.4	
298	25a	80	BPh_3	3.64	6,450	MI > 200; $M_n(^1H)$: 3,310	54.2
299	25a	80	$B(C_6F_5)_3$	0.025	47	$M_n(^1H)$: 3,140	31.6

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^1H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^1H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol.

Table 10 (Cont'd)

Ethylene Polymerizations at 6.9 MPa Pressure Tube Loaded in the Drybox under N_2 Atmosphere (Trichlorobenzene (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^{1}H NMR)	Total Me[d]
300	26a	25	BPh_3	7.89	13,700	MI > 200; M_n(^{1}H): 3,250	69.2
301	26a	25	BPh_3	11.7	17,900	MI > 200; M_n(^{1}H): 3,930	66.6
302	26a	80	$B(C_6F_5)_3$	e	e		
303	27a	25	BPh_3	4.47	7,800	MI: 210; M_n(^{1}H): 8,040	52.7
304	27a	25	BPh_3	7.03	11,500	MI: 108; M_n(^{1}H): 8,230	50.9
305	27a	80	$B(C_6F_5)_3$	0.009	17	M_n(^{1}H): 5,070	27.9
306	28a	25	BPh_3	0.761	1,300	MI: 60; M_n(^{1}H): 19,900	37.1
307	28a	25	BPh_3	0.271	481	M_n(^{1}H): 26,700	31.3
308	28a	80	$B(C_6F_5)_3$	0.006	10	M_n(^{1}H): 6,630	19.8
309	29a	25	$B(C_6F_5)_3$	0.573	994	MI: 0.12; M_n(^{1}H): 4,010	16.2
310	29a	25	BPh_3	e	e		
311	29a	80	$B(C_6F_5)_3$	0.199	360	M_n(^{1}H): 1,650	35.3
312	30a	25	$B(C_6F_5)_3$	2.45	4,160	MI < 0.01; M_n(^{1}H): 8,300	8.1
313	30a	25	BPh_3	e	e		
314	30a	80	$B(C_6F_5)_3$	1.64	2,610	MI: 17; M_n(^{1}H): 3,600	23.0
315	33a	25	BPh_3	0.431	768	M_n(^{1}H): 21,300	3.4
316	33a	25	$B(C_6F_5)_3$	2.35	4,070	MI: 0.13; M_n(^{1}H): 4,270	37.1
317	33a	80	$B(C_6F_5)_3$	0.915	1,540	MI: 36.8: M_n(^{1}H): 1,860	36.1
318	34a	25	$B(C_6F_5)_3$	7.53	11,600	Mn (^{1}H): 3,450	72.4
319	34a	80	$B(C_6F_5)_3$	5.35	7,570	M_w(GPC): 29,100; PDI: 46	113.2
320	36a	25	BPh_3	9.31	15,300	M_w(GPC):461,000;PDI:3.3	8.0
321	36a	80	BPh_3	0.353	564	M_w(GPC):30,000; PDI:4.0	25.8
322	37a	25	BPh_3	0.919	1,650	MI: 0.06; M_n(^{1}H):no olefins	14.4
323	37a	25	BPh_3	0.299	434	M_n(^{1}H): 31,100	15.0
324	37a	80	$B(C_6F_5)_3$	0.269	434	M_n(^{1}H): 5,200	40.4

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol.

Table 10 (Cont'd)

Ethylene Polymerizations at 6.9 MPa Pressure Tube Loaded in the Drybox under N_2 Atmosphere (Trichlorobenzene (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^{1}H NMR)	Total Me[d]
325	38a	25	BPh_3	1.43	2,470	MI: 111; $M_n(^1H)$: 6,150	65.8
326	38a	80	BPh_3	1.55	2,580	MI > 200; $M_n(^1H)$: 2,780	99.2
327	39a	25	$B(C_6F_5)_3$	0.414	814	$M_n(^1H)$: 10,700	7.7
328	39a	25	BPh_3	e	e		
329	39a	25	BPh_3	e	e		
330	39a	80	$B(C_6F_5)_3$	0.758	1,290	MI: 80; $M_n(^1H)$: 5,190	20.1
331	41a	25	BPh_3	0.316	586	$M_n(^1H)$: no olefins	11.5
332	41a	25	$B(C_6F_5)_3$	4.08	6,690	MI < 0.01; Mn (^{1}H): 30,700	30.9
333	41a	80	$B(C_6F_5)_3$	2.26	3,730	MI: 180; $M_n(^1H)$: 9,960	36.9
334	43a	25	BPh_3	e	e		
335	43a	25	$B(C_6F_5)_3$	0.53	918	$M_n(^1H)$: 3,600	36.6
336	43a	80	BPh_3	e	e		
337	43a	80	$B(C_6F_5)_3$	0.054	93	$M_n(^1H)$: 2,960	32.0
338	44a	25	$B(C_6F_5)_3$	0.167	291	M_w(GPC): 136,000; PDI:18	25.4
339	44a	80	$B(C_6F_5)_3$	0.019	34	Mn (^{1}H): 5,150	43.3
340	45a	25	$B(C_6F_5)_3$	0.026	43	$M_n(^1H)$: 5,150	8.6
341	45a	80	$B(C_6F_5)_3$	trace	trace	$M_n(^1H)$: 6,310	14.2

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol.

Table 11
Ethylene Polymerizations at 6.9 MPa Pressure Tube Loaded in the Drybox under N_2 Atmosphere (p-Xylene, (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^1H NMR)	Total Me[d]
342	3a[h]	25	BPh_3	20.2	12,000	MI: 2.6	
343	3a[g]	25	BPh_3	0.19	366		
344	3a[g]	25	$B(C_6F_5)_3$	0.48	1,160	$M_n(^1H)$: 27,100	24.4
345	6a[h]	80	BPh_3	11.1	6,610	MI: 105; $M_n(^1H)$: 9,090	31.1
346	6a[h]	80	$B(C_6F_5)_3$	6.90	4,100	MI: >200; $M_n(^1H)$: 3,170	63.4
347	6a[g]	80	$B(C_6F_5)_3$	3.47	8,470	MI: 58.8; $M_n(^1H)$: 6,880	34.5

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^1H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^1H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol.

Table 12
Ethylene Polymerizations at 6.9 MPa Pressure Tube Loaded in the Drybox under N_2 Atmosphere (Cyclohexane, (5 mL), 18 h)

Ex.	Cmpd[f]	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^1H NMR)	Total Me[d]
348	3a[g]	25	BPh_3	0.52	1,160		
349	6a[h]	80	BPh_3	10.6	6,270	MI: 135; $M_n(^1H)$: 7,410	33.8
350	6a[g]	80	BPh_3	7.07	16,810	MI: 129; $M_n(^1H)$: 8,800	27.7

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^1H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^1H NMR analysis. [e]PE was not obtained in isolable quantities. [f]0.02 mmol unless noted otherwise. [g]0.015 mmol. [h]0.06 mmol.

Table 13
Ethylene Polymerizations at 1.4 MPa
Pressure Tube Loaded in the Drybox under N_2 Atmosphere
(Trichlorobenzene (5 mL), 0.02 mmol Cmpd, 18 h)

Ex.	Cmpd	Temp (°C)	Lewis Acid[a]	PE(g)	PE(TO)[b]	M.W.[c] (MI, GPC, and/or ^{1}H NMR)	Total Me[d]
351	3a	25	BPh_3	1.71	2,540	MI: 0.26; $M_n(^1H)$: 64,600	17.3
352	4a	25	BPh_3	2.87	5,000	MI: 92; $M_n(^1H)$: 15,300	40.3
353	6a	25	$B(C_6F_5)_3$	2.31	3,760	MI: 1; $M_n(^1H)$: 11,700	55.0
354	8a	25	$B(C_6F_5)_3$	2.10	3,440	MI: 123; $M_n(^1H)$:5,570	81.5
355	9a	25	$B(C_6F_5)_3$	1.53	2,730	$M_n(^1H)$: 4,850	112.3
356	14a	25	$B(C_6F_5)_3$	1.18	2,080	MI: 7.5; $M_n(^1H)$: 4,730	53.3
357	21a	25	BPh_3	1.58	2,670	MI: 1.5; $M_n(^1H)$: 14,700	39.9
358	22a	25	BPh_3	2.94	4740	MI > 200; $M_n(^1H)$: 4,580	73.7
359	25a	25	BPh_3	1.18	2,060	MI: 6.6; $M_n(^1H)$: 5,020	110.6
360	26a	25	BPh_3	2.41	4,040	MI > 200; $M_n(^1H)$: 3,870	73.6

[a]Two equiv. [b]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [c]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [d]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [e]PE was not obtained in isolable quantities.

Table 14
Ethylene Polymerizations Using Nickel Methyl Initiators:
Effect of Lewis Acid on Initiation/Productivity
(6.9 MPa, 0.02 mmol Cmpd, Trichlorobenzene (5 mL), 18 h)

Ex.	Cmpd	Temp (°C)	Lewis Acid (equiv)	PE(g)	PE(TO)[a]	M.W.[b] (MI, GPC, and/or ^{1}H NMR)	Total Me[c]
361	50[d]	25	none	trace	trace		
362	50[d]	80	none	0.189	307	$M_n(^1H)$: 5,840	39.4
363	50	25	BPh_3 (2)	0.126	201		
364	50	80	$B(C_6F_5)_3$ (2)	0.074	124		
365	50	25	BPh_3 (10)	4.41	7,590		
366	50	80	BPh_3 (10)	3.01	5,220	M_w(GPC):17,900;PDI:6	

[a]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [b]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [c]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [d]Under the same reaction conditions (e.g., no Lewis acid present), nickel compounds **51** - **54** gave analogous results: no polymer was isolated, but the ^{1}H NMR spectra showed a $-(CH_2)_n-$ resonance.

Examples 367 - 369

Cyclopentene Oligomerizations

General Procedure for Cyclopentene Oligomerizations. In the drybox under a nitrogen atmosphere, the nickel compound (0.03 mmol) was placed in a vial. Next, 5 mL of toluene was added to the vial followed by 1.3 mL of cyclopentene. $B(C_6F_5)_3$ (40 mg) was then added to the vial. The reaction mixture was mixed for 3 d on a vortexer and then removed from the drybox and added to 100 mL of stirring methanol. No polymer precipitated. GC analysis was carried out on the organic layer. The results are reported in Table 15 below.

Table 15
Cyclopentene Oligomerizations

Ex.	Cmpd	GC Analysis
367	31a	dimers through heptamers observed
368	32a	dimers through heptamers observed
369	47b	dimers through heptamers observed

Examples 370 - 375

Ethylene/Ethyl 4-Pentenoate Polymerizations

General Procedure for Ethylene/Ethyl 4-Pentenoate Polymerizations. In a nitrogen-filled drybox, the nickel compound (0.06 mmol) and the Lewis acid (5 equiv) were placed together in a glass insert. The insert was cooled to -30 °C in the drybox freezer. 5 mL of cold ethyl 4-pentenoate was added to the cold insert, and the insert was recooled in the drybox freezer. The cold inserts were removed from the drybox and placed under a nitrogen purge in a pressure tube, which was then sealed and pressurized to 6.9 MPa of ethylene and mechanically shaken for 18 h. The pressure was then released and the glass insert was removed from the pressure tube and the polymer was precipitated in MeOH, collected on a frit, and dried in vacuo. Characteristic NMR resonances of the copolymer include the 4.01 OCH_2 resonance in the ^1H NMR and the 59.7 OCH_2 resonance and ~172.4 C=O resonances in the ^{13}C NMR spectrum.

Table 16
Ethylene/Ethyl 4-Pentenoate (E-4-P) Polymerizations

Ex.	Cmpd	Lewis Acid	Temp (°C)	Polymer (g)	DSC/GPC
370	3a	BPh_3	25	2.35	DSC: T_m = 111 °C
		^{13}C NMR: 0.59 mole percent E-4-P Incorp.; Branching per 1000 CH_2's: Total methyls (27.3), Methyl (23.7), Ethyl (1.7), Propyl (0), Butyl (0.8), Amyl (2.4), Hex and greater and end of chains (5.4), Am and greater and end of chains (1.9), Bu and greater and end of chains (1.8)			
371	21a	BPh_3	25	0.586	DSC: T_m = 115 °C
		^{13}C NMR: 0.26 mole percent E-4-P Incorp.; Branching per 1000 CH_2's: Total methyls (25.0), Methyl (19.3), Ethyl (2.1), Propyl (0.0), Butyl (1.2), Amyl (0.3), Hex and greater and end of chains (3.1), Am and greater and end of chains (4.1), Bu and greater and end of chains 3.6)			

Table 16 (Cont'd)
Ethylene/Ethyl 4-Pentenoate (E-4-P) Polymerizations

Ex.	Cmpd	Lewis Acid	Temp (°C)	Polymer (g)	DSC/GPC
372	8a	$B(C_6F_5)_3$	25	0.254	DSC: T_m = 124 °C, 96 °C
		^{13}C NMR: 0.64 mole percent E-4-P Incorp.; Branching per 1000 CH_2's: Total methyls (47.8), Methyl (35.8), Ethyl (3.7), Propyl (0.0), Butyl (3.1), Amyl (3.8), Hex and greater and end of chains (8.7), Am and greater and end of chains (10.2), Bu and greater and end of chains (8.3)			
373	3a	BPh_3	80	0.468	
		^{13}C NMR: 1.94 mole percent E-4-P Incorp.; Branching per 1000 CH_2's: Total methyls (67.0), Methyl (50.7), Ethyl (6.3), Propyl (0.0), Butyl (3.7), Amyl (7.3), Hex and greater and end of chains (18.6), Am and greater and end of chains (8.4), Bu and greater and end of chains (9.9)			
374	21a	BPh_3	80	0.312	
		^{13}C NMR: 1.67 mole percent E-4-P Incorp.; Branching per 1000 CH_2's: Total methyls (73.9), Methyl (47.9), Ethyl (9.2), Propyl (0.0), Butyl (0.0), Amyl (6.1), Hex and greater and end of chains (16.2), Am and greater and end of chains (15.7), Bu and greater and end of chains (16.8)			
375	8a	$B(C_6F_5)_3$	80	0.232	GPC (THF, 35 °C): M_w = 5,130, PDI = 1.7; DSC: T_m: 117 °C, 46 °C
		^1H NMR: 1.6 mole percent E-4-P Incorp.; Branching per 1000 CH_2's: Total methyls (94)			

Examples 376-381

General Procedure for Ethylene Polymerizations of Table 17:

Ethylene Polymerizations in the Parr® Reactor

Procedure. Prior to conducting the polymerization, the Parr® reactor flushed with nitrogen, heated under vacuum overnight, and then allowed to cool to room temperature. In the drybox, a glass vial was loaded with the nickel compound, Lewis acid and solvent and then capped with a rubber septum.

The solution of the nickel complex and Lewis acid was then transferred to a 100 mL Parr reactor under vacuum, and the reactor was pressurized with ethylene and the reaction mixture was mechanically stirred. After the stated reaction time, the ethylene pressure was released, and the polymer was precipitated by adding the reaction mixture to a solution of MeOH (~100 mL) and concentrated HCl (~1-3 mL). The polymer was then collected on a frit and rinsed with HCl, MeOH, and acetone. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. The polymer yield and characterization were then obtained.

Table 17
Ethylene Polymerizations in the Parr Reactor
(0.02 mmol Cmpd, Trichlorobenzene (35 mL))

Ex.	Cmpd	Time (h)	Press. (MPa)	LewisAcid (equiv)	PE(g)	PE(TO)[a]	M.W.[b] (MI, GPC, and/or ^{1}H NMR)	Total Me[c]
376	**6a**	9.9	5.5	$B(C_6F_5)_3$/2	7.46	12,400	M_n(^{1}H):no olefins	34.4
377	**6a**	0.5	5.5	$B(C_6F_5)_3$/2	3.5	5,940	M_n(^{1}H):no olefins	40.3
378	**6a**	6.5	5.5	$B(C_6F_5)_3$/2	9.30	15,500	M_n(^{1}H):no olefins	39.2
379	**6a**	4.8	1.4	$B(C_6F_5)_3$/2	0.26	394	M_n(^{1}H):no olefins	32.6
380	**3a**	6.0	3.5	BPh_3/5	3.57	5,560	M_n(^{1}H):no olefins	19.1
381	**6a**	6.6	3.5	$B(C_6F_5)_3$/5	1.52	2,480	M_n(^{1}H):no olefins	29.0

[a]TO: number of turnovers per metal center = (moles ethylene consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst). Calculations are based upon the exact amount of catalyst used. [b]M.W.: Molecular weight of the polymer or oligomers as determined by melt index (MI: g/10 min at 190 °C), GPC (molecular weights are reported versus polystyrene standards; conditions: Waters 150C, trichlorobenzene at 150 °C, Shodex columns at-806MS 4G 734/602005, RI detector), and/or ^{1}H NMR (olefin end group analysis). [c]Total number of methyl groups per 1000 methylene groups as determined by ^{1}H NMR analysis. [d]Under the same reaction conditions (e.g., no Lewis acid present), nickel compounds **51** - **54** gave analogous results: no polymer was isolated, but the ^{1}H NMR spectra showed a $-(CH_2)_n-$ resonance.

Examples 382-437

General Procedure for Ethylene (28-35 kPa) Polymerizations of Table 18

Procedure. In the drybox, a glass Schlenk flask was loaded with the nickel compound, Lewis acid, solvent and a stir bar. The flask was then capped with a rubber septum and the stopcock was closed prior to

removing the flask from the drybox. The flask was then attached to the ethylene line where it was evacuated and backfilled with ethylene. The reaction mixture was stirred under ethylene for the stated reaction time, the ethylene pressure was then released, and the polymer was precipitated by adding the reaction mixture to a solution of MeOH (~100 mL) and concentrated HCl (~1-3 mL). The polymer was then collected on a frit and rinsed with MeOH. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. The polymer yield and characterization were then obtained.

Table 18

Ethylene Polymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Solvent (mL)[b]	PE(g)	PE(TO)
382	1a	$B(C_6F_5)_3$/20	25.0	Toluene (35)	*a*	*a*
383	1a	MAO-IP/90	0.5	Toluene (35)	0.924	1,040
			Description: White rubbery solid.			
384	2a	MAO-IP/86	0.5	Toluene (35)	0.534	577
			Description: White, soft, slightly rubbery solid.			
385	3a	BPh_3/5	26.3	Toluene (35)	*a*	*a*
386	3a	BPh_3/20	23.5	Toluene (35)	0.662	787
			Description: Slightly sticky, clear, colorless amorphous solid. ^1H NMR (C_6D_6, rt) 99.6 total Me/1000CH_2			
387	3a	BPh_3/50	23.5	Toluene (35)	0.110	131
			Description: Clear, colorless sticky viscous oil. ^1H NMR (C_6D_6, rt) 98.6 total Me/1000CH_2			
388	3a	BPh_3/100	23.5	Toluene (35)	0.021	25
			Description: Light yellow, clear amorphous solid/oil. ^1H NMR (C_6D_6, rt) 102.7 total Me/1000CH_2			
389	3a	$B(C_6F_5)_3$/20	32.4	Toluene (35)	0.042	50
			Description: White powder.			
390	3a	$BF_3 \cdot Et_2O$/50	25.5	Toluene (35)	*a*	*a*
391	4a	BPh_3/50	23.5	Toluene (35)	0.261	310
			Description: Clear, amorphous gummy solid. ^1H NMR (C_6D_6, rt) 107.4 total Me/1000CH_2			

[a]Only a trace of polymer or no polymer was isolated. [b]1,2,4-Trichlorobenzene is abbreviated as 1,2,4-TCB.

Table 18 (Cont'd)

Ethylene Polymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Solvent (mL)[b]	PE(g)	PE(TO)
392	4a	BPh_3/100	37.2	Toluene (35)	0.797	950
Description: Soft, white powder/solid.						
393	5a	BPh_3/5	26.3	Toluene (35)	[a]	[a]
394	5a	BPh_3/50	23.5	Toluene (35)	0.054	64
Description: White slightly sticky, partially amorphous solid.						
395	5a	BPh_3/50	26.4	Toluene (35)	0.065	77
Description: Clear/white partial powder/partial amorphous solid.						
396	6a	$B(C_6F_5)_3$/5	26.4	Toluene (35)	0.15	180
Description: Brown sticky amorphous solid. ^1H NMR (C_6D_6, rt): 105.4 Total Me/1000 CH_2						
397	6a	$B(C_6F_5)_3$/20	26.4	Toluene (35)	7.38	8,760
Description: White, slightly rubbery or spongy powder. ^{13}C NMR: Branching per 1000 CH_2's. Total methyls (59.8), methyl (38.5), ethyl (10.4), propyl (1.6), butyl (2.4), hexyl and greater and end of chains (7.0), amy and greater and end of chains (7.9), butyl and greater and end of chains (9.3).						
398	6a	BPh_3/100	17.0	Toluene (35)	0.17	200
Description: White soft powder.						
399	6a	$BF_3 \cdot Et_2O$/50	25.5	Toluene (35)	[a]	[a]
400	6a	$Al(O\text{-}i\text{-}Pr)_3$/20	22.4	Toluene (35)	[a]	[a]
401	6a	PMAO-IP/28	25.1	Toluene (35)	[a]	[a]

[a]Only a trace of polymer or no polymer was isolated. [b]1,2,4-Trichlorobenzene is abbreviated as 1,2,4-TCB.

Table 18 (Cont'd)

Ethylene Polymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Solvent (mL)[b]	PE(g)	PE(TO)
402	**7a**	$B(C_6F_5)_3$/20	24.1	Toluene (35)	1.04	1,180
Description: White powder.						
403	**8a**	$B(C_6F_5)_3$/5	25.4	Toluene (35)	1.45	1,730
Soft partial powder/partial amorphous solid. ^{1}H NMR (C_6D_6, rt): 118.3 Total Me/1000 CH_2						
404	**8a**	BPh_3/100	17.0	Toluene (35)	0.016	19
Description: Tan powder.						
405	**8a**	$B(C_6F_5)_3$/20	23.1	Toluene (35)	2.82	3,350
Description: Brown amorphous sticky solid. ^{1}H NMR (C_6D_6, rt): 143.0 Total Me/1000 CH_2						
406	**9a**	$B(C_6F_5)_3$/5	26.4	Toluene (35)	0.018	21
Description: Brown partial oil, partial amorphous solid.						
407	**9a**	$B(C_6F_5)_3$/20	23.1	Toluene (35)	6.99	8,300
Description: Brown amorphous sticky solid. ^{1}H NMR (C_6D_6, rt): 174.4 Totalt Me/1000 CH_2						
408	**10a**	BPh_3/20	24.2	Toluene (35)	1.43	1,700
Description: White powder.						
409	**12a**	BPh_3/20	25.0	Toluene (35)	0.749	890
Description: White powder.						
410	**12a**	$B(C_6F_5)_3$/10	22.5	Toluene (35)	a	a
411	**14a**	$B(C_6F_5)_3$/20	25.5	Toluene (35)	0.97	1,150
Description: White, stringy powder						

[a]Only a trace of polymer or no polymer was isolated. [b]1,2,4-Trichlorobenzene is abbreviated as 1,2,4-TCB.

Table 18 (Cont'd)

Ethylene Polymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Solvent (mL)[b]	PE(g)	PE(TO)
412	**15a**	$B(C_6F_5)_3$/10	22.5	Toluene (35)	0.106	126
Description: Slightly rubbery off-white solid.						
413	**17a**	$B(C_6F_5)_3$/20	25.5	Toluene (35)	2.08	2,470
Description: Soft white powder.						
414	**21a**	BPh_3/5	25.4	Toluene (35)	1.88	2,230
Description: White, somewhat rubbery powder.						
415	**21a**	BPh_3/20	26.4	Toluene (35)	1.73	2,060
Description: White powder.						
416	**21a**	BPh_3/50	26.4	Toluene (35)	0.631	750
Description: White powder.						
417	**21a**	BPh_3/100	21.4	1,2,4-TCB (20)	0.474	563
Description: White powder.						
418	**21b**	BPh_3/100	21.4	1,2,4-TCB (20)	0.156	185
419	**22a**	BPh_3/100	37.2	Toluene (35)	0.777	920
Description: White powder.						
420	**23a**	BPh_3/20	26.0	Toluene (35)	0.409	473
Description: Almost clear, sticky amorphous oil/solid.						
421	**24a**	$B(C_6F_5)_3$/10	22.5	Toluene (35)	*a*	*a*

[a]Only a trace of polymer or no polymer was isolated. [b]1,2,4-Trichlorobenzene is abbreviated as 1,2,4-TCB.

Table 18 (Cont'd)

Ethylene Polymerizations at 28035 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Solvent (mL)[b]	PE(g)	PE(TO)
422	**24a**	BPh_3/50	22.4	Toluene (35)	0.374	444
		Description: White powder.				
423	**25a**	BPh_3/50	24.2	Toluene (35)	1.47	1,750
		Description: White, slightly rubbery powder.				
424	**27a**	BPh_3/20	26.0	Toluene (35)	0.856	992
		Description: Amorphous, slightly sticky, waxy, clear solid. ^1H NMR (C_6D_6, rt) 90.0 total $Me/1000CH_2$				
425	**30a**	$B(C_6F_5)_3$/20	24.2	Toluene (25)	0.65	770
		Description: White powder.				
426	**34a**	$B(C_6F_5)_3$/20	23.1	Toluene (35)	5.75	6,830
		Description: Tan amorphous solid. ^1H NMR (C_6D_6, rt) 182.0 Total Me/1000 CH_2. Mn ~1,980				
427	**36a**	BPh_3/20	25.6	Toluene (35)	1.32	1,570
		Description: White powder.				
428	**36a**	$B(C_6F_5)_3$/10	24.3	Toluene (35)	0.11	130
		Description: Tan powder.				
429	**37a**	BPh_3/20	23.8	Toluene (35)	0.486	576
430	**38a**	BPh_3/20	26.0	Toluene (35)	0.024	28
		Description: Clear, amorphous, very slightly sticky solid ^1H NMR (C_6D_6, rt) 91.2 total $Me/1000CH_2$				
431	**39a**	$B(C_6F_5)_3$/20	22.6	Toluene (20)	0.244	290
		Description: White powder.				

[a]Only a trace of polymer or no polymer was isolated. [b]1,2,4-Trichlorobenzene is abbreviated as 1,2,4-TCB.

Table 18 (Cont'd)

Ethylene Polymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Solvent (mL)[b]	PE(g)	PE(TO)
432	**39a**	BPh_3/200	23.8	Toluene (35)	*a*	*a*
433	**41a**	$B(C_6F_5)_3$/5	25.4	Toluene (35)	0.059	70
				Description: White powder.		
434	**41a**	$B(C_6F_5)_3$/20	22.4	Toluene (35)	1.73	2,060
				Description: White powder.		
435	**50**	BPh_3/100	21.4	1,2,4-TCB (20)	1.06	1,260
				Description: White powder.		
436	**52**	BPh_3/100	21.4	1,2,4-TCB (20)	1.21	1,440
				Description: White powder.		
437	**52**	BPh_3/100	23.1	Toluene (35)	1.40	1,660
				Description: White powder.		

[a]Only a trace of polymer or no polymer was isolated. [b]1,2,4-Trichlorobenzene is abbreviated as 1,2,4-TCB.

Example 438

Ethylene Polymerization Using (acac)Ni(Et)PPh_3 Precursor at 6.9 MPa

In the drybox, a glass insert was loaded with (acac)Ni(Et)PPh_3 (26.9 mg, 0.06 mmol) and [2-(NaO)-3,5-(*t*-Bu)$_2$-C_6H_2-C(Me)=NAr (Ar = 2,6-(*i*-Pr)$_2$-C_6H_3) · 0.5 THF] (25.8 mg, 1 equiv). The insert was cooled to -35 °C in the drybox freezer, 5 mL of C_6D_6 was added to the cold insert, and the insert was cooled again. BPh_3 (29.1 mg, 2 equiv) was added to the cold solution, and the insert was then capped and sealed and cooled again. Outside of the drybox, the cold insert was placed under a nitrogen purge into the pressure tube. The pressure tube was sealed, placed under ethylene (6.9 MPa), and allowed to warm to rt as it was shaken mechanically for approximately 18 h. Polyethylene (16.5 g, 9,820 TO)

was isolated as a powder following precipitation from methanol.

Example 439

Ethylene Polymerization Using $NiBr_2$ Precursor at 28-35 MPa

The sodium salt of the ligand of Example 1 (1.01 g, 2.23 mmol), e.g.

$$ArN{=}C\text{-}CH_2CH_2CH_2\text{-}CH{=}C\text{-}N(Na)Ar\ [Ar = 2{,}6\text{-}(\textit{i}\text{-}Pr)_2C_6H_3]$$

was placed in a round bottom flask in the drybox together with 487 mg (2.23 mmol) of $NiBr_2$. THF (20 mL) was added and the solution was stirred for ~2 months. The THF was removed in vacuo and the product was dissolved in CH_2Cl_2 and the resulting solution was filtered. The solvent was removed and the product was dried in vacuo. An orange powder (488 mg) was isolated. (In addition to CD_2Cl_2, the product was also soluble in C_6D_6. ^1H NMR spectra in both solvents were complex.)

In the drybox, a glass Schlenk flask was loaded with the resulting orange nickel compound (17 mg, ~0.03 mmol), 35 mL of toluene and a stir bar. The flask was then capped with a rubber septum and the stopcock was closed prior to removing the flask from the drybox. The flask was then attached to the ethylene line where it was evacuated and backfilled with ethylene. MAO-IP (2 mL, ~94 equiv) was added to the flask via cannula. The reaction mixture was stirred under ethylene for 3.5 h, the ethylene pressure was then released, and the polymer was precipitated by adding the reaction mixture to a solution of MeOH (~100 mL) and concentrated HCl (~1-3 mL). The polymer was then collected on a frit and rinsed with MeOH. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. A white polyethylene film (5.09 g, ~6050 TO) was isolated.

Examples 440-468

Ligand Syntheses

Ligand syntheses and deprotonations were carried out according to the general procedures given below and under Examples 1-16 (see above) unless stated otherwise.

Example 440

$[2\text{-(OH)-3,5-Cl}_2\text{-C}_6\text{H}_2]\text{-C(Me)=NAr}$ $[\text{Ar} = 2,6\text{-(}i\text{-Pr)}_2\text{-C}_6\text{H}_3]$

The general procedure for imine synthesis was followed using 10.03 g (48.9 mmol) of 3′,5′-dichloro-2′-hydroxyacetophenone and 11.27 g (1.30 equiv) of 2,6-diisopropylaniline. A yellow powder (15.35 g, 86.2%) was isolated: ^{1}H NMR ($CDCl_3$) δ 7.46 (d, 1, Ar′: H), 7.44 (d, 1, Ar′: H), 7.14 (m, 3, Ar: H), 2.64 (septet, 2, C*H*Me_2), 2.12 (s, 3, N=C(*Me*)), 1.08 and 1.04 (d, 6 each, CH*MeMe′*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.59 equiv of THF coordinated.

Example 441

$[2\text{-(OH)-3,5-Cl}_2\text{-C}_6\text{H}_2]\text{-C(Me)=NAr}$ $[\text{Ar} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3]$

The general procedure for imine synthesis was followed using 10.681 g (52.1 mmol) of 3′,5′-dichloro-2′-hydroxyacetophenone and 8.21 g (1.30 equiv) of 2,6-dimethylaniline. A yellow powder (7.61 g, 47.4) was isolated: ^{1}H NMR ($CDCl_3$) δ 7.57 (d, 1, Ar′: H), 7.52 (d, 1, Ar′: H), 7.15 (d, 2, Ar: H_m), 7.08 (t, 1, Ar: H_p), 2.21 (s, 3, N=C*Me*), 2.10 (s, 6, Ar: *Me*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.59 equiv of THF coordinated.

Example 442

$[2\text{-(OH)-3,5-Cl}_2\text{-C}_6\text{H}_2]\text{-C(Me)=NAr}$ $[\text{Ar} = 2\text{-(}t\text{-Bu)-C}_6\text{H}_4]$

The general procedure for imine synthesis was followed using 10.41 g (50.8 mmol) of 3′,5′-dichloro-2′-hydroxyacetophenone and 9.85 g (1.30 equiv) of 2-*t*-butylaniline. A yellow powder (15.30 g, 89.6%, 2 crops) was isolated: ^{1}H NMR ($CDCl_3$) δ 7.55 (d, 1,

Ar': H), 7.52 (d, 1, Ar': H), 7.50 (d, 1, Ar: H), 7.25 (t, 1, Ar: H), 7.22 (t, 1, Ar: H), 6.52 (d, 1, Ar: H), 2.31 (s, 3, Me), 1.36 (s, 9, CMe_3).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.16 equiv of THF coordinated.

Example 443

$[2\text{-(OH)-3,5-Br}_2\text{-C}_6\text{H}_2]\text{-CH=NAr}$ $[\text{Ar} = 2,6\text{-(}i\text{-Pr)}_2\text{-C}_6\text{H}_3]$

The general procedure for imine synthesis was followed using 3.23 g (11.5 mmol) of 3,5-dibromosalicylaldehyde and 2.66 g (1.30 equiv) of 2,6-diisopropylaniline. A yellow powder (3.10 g, 61.4%) was isolated: ^{1}H NMR ($CDCl_3$) 8.21 (s, 1, N=C*H*), 7.81 (d, 1, Ar': H), 7.45 (d, 1, Ar': H), 7.22 (s, 3, Ar: H), 2.94 (septet, 2, C*H*Me_2), 1.18 (d, 12, CH*Me*$_2$).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.7 equiv of THF coordinated.

Example 444

$[2\text{-(OH)-3,5-Br}_2\text{-C}_6\text{H}_2]\text{-C(Me)=NAr}$ $[\text{Ar} = 2,6\text{-(}i\text{-Pr)}_2\text{-C}_6\text{H}_3]$

The general procedure for imine synthesis was followed using 10.84 g (36.9 mmol) of 3',5'-dibromo-2'-hydroxyacetophenone and 8.50 g (1.30 equiv) of 2,6-diisopropylaniline. A yellow powder (13.16 g, 78.7%) was isolated: ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 1, Ar': H), 7.73 (d, 1, Ar': H), 7.26 (m, 3, Ar: H), 2.76 (septet, 2, C*H*Me_2), 2.24 (s, 3, *Me*), 1.19 and 1.18 (d, 6 each, CH*MeMe'*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.54 equiv of THF coordinated.

Example 445

$[2\text{-(OH)-3,5-Br}_2\text{-C}_6\text{H}_2]\text{-C(Me)=NAr}$ $[\text{Ar} = 2,6\text{-Me}_2\text{-C}_6\text{H}_3]$

The general procedure for imine synthesis was followed using 10.43 g (35.5 mmol) of 3',5'-dibromo-2'-hydroxyacetophenone and 5.59 g (1.30 equiv) of 2,6-dimethylaniline. A yellow powder (11.6 g) was isolated. The ^{1}H NMR spectrum of the initially

isolated product showed that it was contaminated by the hydroxyacetophenone. The product was repurified by washing with more methanol, dissolving in CH_2Cl_2 and drying over Na_2SO_4, filtering and evaporating the solvent. A yellow powder (5.60 g) was isolated. The product mixture was now 12.7% of the starting aldehyde. The remainder is the desired imine product: ^{1}H NMR ($CDCl_3$) δ 7.78 (d, 1, Ar′: H), 7.71 (d, 1, Ar′: H), 7.11 (d, 2, Ar: H_m), 7.05 (t, 1, Ar: H_p), 2.18 (s, 3, N=C*Me*), 2.05 (s, 6, Ar: *Me*).

The sodium salt was synthesized according to the above general procedure and is clean and consistent with the desired product (no hydroxyacetophenone impurities present): ^{1}H NMR (THF-d_8): 0.81 equiv of THF coordinated.

Example 446

[2-(OH)-3,5-Br_2-C_6H_2]-C(Me)=NAr [Ar = 2-(*t*-Bu)-C_6H_4]

The general procedure for imine synthesis was followed using 10.04 g (34.2 mmol) of 3′,5′-dibromo-2′-hydroxyacetophenone and 6.63 g (1.30 equiv) of 2-*t*-butylaniline. A yellow powder (12.63 g, 86.9%) was isolated: ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 1, Ar′: H), 7.72 (d, 1, Ar′: H), 7.51 (d, 1, Ar: H), 7.27 (t, 1, Ar: H), 7.22 (t, 1, Ar: H), 6.51 (d, 1, Ar: H), 2.31 (s, 3, N=C*Me*), 1.37 (s, 9, C*Me*$_3$).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): trace THF coordinated.

Example 447

[2-(OH)-3,5-(*t*-Bu)$_2$$C_6H_2$]-CH=NAr [Ar = 2-(*t*-Bu)-C_6H_4]

The general procedure for imine synthesis was followed using 4.12 g (17.6 mmol) of 3,5,-di-*t*-butyl-2-hydroxybenzaldehyde and 3.15 g (1.20 equiv) of 2-*t*-butylaniline. The desired imine product was isolated as a yellow powder: ^{1}H NMR ($CDCl_3$) δ 8.36 (s, 1, N=C*H*), 7.40 (d, 1, Ar′: H), 7.36 (d, 1, Ar: H), 7.18 (t, 1, Ar: H), 7.15 (d, 1, Ar′: H), 7.13 (t, 1, Ar: H),

6.80 (d, 1, Ar: H), 1.42, 1.37 and 1.26 (s, 9 each, C*Me*$_3$, C'*Me*$_3$, C''*Me*$_3$).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): ~1 equiv of THF coordinated.

Example 448

$[2\text{-}(OH)\text{-}3,5\text{-}(t\text{-}Bu)_2C_6H_2]\text{-}CH{=}NAr$ $[Ar = 2\text{-}Aza\text{-}C_5H_4]$

The general procedure for imine synthesis was followed using 3.02 g (12.9 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 1.46 g (1.20 equiv) of 2-amino-pyridine. An orange powder (0.552 g, 13.8%) was isolated: ^{1}H NMR ($CDCl_3$) δ 9.47 (s, 1, N=C*H*), 8.51 (m, 1, Py: H), 7.77 (m, 1, Py: H), 7.48 (d, 1, Ar': H), 7.35 (d, 1, Ar': H), 7.33 (m, 1, Py: H), 7.20 (m, 1, Py: H), 1.48 (s, 9, C*Me*$_3$), 1.34 (s, 9, C'*Me*$_3$).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.2 equiv of THF coordinated.

Example 449

$[2\text{-}(OH)\text{-}3,5\text{-}(t\text{-}Bu)_2C_6H_2]\text{-}CH{=}NAr$ $[Ar = 2\text{-}Aza\text{-}6\text{-}Me\text{-}C_5H_3]$

The general procedure for imine synthesis was followed using 3.46 g (14.7 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 1.91 g (1.20 equiv) of 2-amino-3-picoline. The first crop isolated as a precipitate from methanol was an orange powder (1.18 g). This crop was not clean and was discarded, although some of the desired product was present as a minor component. The remaining methanol solution was allowed to slowly evaporate to give orange crystals. The methanol was decanted off of the crystals and the standard work-up procedure was followed. An orange powder (0.813 g) was isolated, and the NMR spectrum of this second crop was clean and consistent with the desired product: ^{1}H NMR ($CDCl_3$) δ 9.45 (s,1, N=C*H*), 8.34 (d, 1, Py: H), 7.60 (d, 1, Py: H), 7.48 (d, 1, Ar': H), 7.38 (d, 1, Ar': H), 7.13 (dd, 1, Py: H), 2.49 (s, 3, *Me*), 1.5 (s, 9, C*Me*$_3$), 1.34 (s, 9, C'*Me*$_3$).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.4 equiv of THF coordinated.

Example 450

$[2\text{-(OH)-}3,5\text{-}(t\text{-Bu})_2C_6H_2]\text{-CH=NCHPh}_2$

The general procedure for imine synthesis was followed using 3.00 g (12.8 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 2.60 g (1.11 equiv) of aminodiphenylmethane. A yellow powder (2.85 g, 55.7%) was isolated: ^{1}H NMR ($CDCl_3$) δ 8.50 (s, 1, N=C*H*), 7.42 (d, 1, Ar′: H), 7.40 - 7.23 (m, 10, CPh_2), 7.11 (d, 1, Ar′: H), 5.63 (s, 1, C*H*Ph_2), 1.48 and 1.32 (s, 9 each, CMe_3 and C′Me_3).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 1 equiv of THF coordinated.

Example 451

$[2\text{-(OH)-}3,5\text{-}(t\text{-Bu})_2C_6H_2]\text{-CH=NR}$ [R = 1,2,3,4-tetrahydro-1-naphthyl]

The general procedure for imine synthesis was followed using 3.08 g (13.1 mmol) of 3,5-di-*t*-butyl-2-hydroxybenzaldehyde and 2.32 g (1.20 equiv) of 1,2,3,4-tetrahydro-1-naphthylamine. A yellow powder (3.97 g, 83.4%) was isolated: ^{1}H NMR ($CDCl_3$) δ 8.45 (s, 1, N=C*H*), 7.39 (d, 1, Ar′: H), 7.22 - 7.04 (m, 5, Ar: H, Ar′: H), 4.53 (m, 1, NC*H*$CH_2CH_2CH_2$), 2.88 (m, 2, $NCHCH_2CH_2CH_2$), 2.14 - 1.79 (m, 4, $NCHCH_2CH_2CH_2$), 1.42 (s, 9, CMe_3), 1.32 (s, 9, C′Me_3).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.6 equiv of THF coordinated.

Example 452

$[2\text{-(OH)-}3,5\text{-}(NO_2)_2C_6H_2]\text{-CH=NAr}$ [Ar = 2-(*t*-Bu)-C_6H_4]

The general procedure for imine synthesis was followed using 3.05 g (14.4 mmol) of 3,5-dinitrosalicylaldehyde and 2.57 g (1.20 equiv) of 2-*t*-butylaniline. A yellow powder was isolated: ^{1}H NMR ($CDCl_3$) δ 8.94 (s, 1, N=C*H*), 8.54 (d, 1, Ar′: H), 8.50

(d, 1, Ar′: H), 7.49 (d, 1, Ar: H), 7.35 (t, 1, Ar: H), 7.31 (t, 1, Ar: H), 7.02 (d, 1, Ar: H), 1.40 (s, 9 CMe_3).

The sodium salt was synthesized according to the above general procedure: [1]H NMR (THF-d_8): 0.79 equiv of THF coordinated.

Example 453

$[2\text{-}(OH)\text{-}3,5\text{-}(NO_2)_2C_6H_2]\text{-}CH{=}NAr$ [Ar = 2-Me-6-Cl-C_6H_3]

The general procedure for imine synthesis was followed using 1.56 g (7.33 mmol) of 3,5-dinitrosalicylaldehyde and 1.25 g (1.20 equiv) of 2-chloro-6-methylaniline. An orange powder (1.35 g, 55.0%) was isolated: [1]H NMR ($CDCl_3$) δ 15.96 (br s, 1, O*H*), 8.71 (s, 1, N=C*H*), 8.60 (d, 1, H_{aryl}), 7.50 - 7.15 (m, 4, H_{aryl}), 2.36 (s, 1, *Me*).

The sodium salt was synthesized according to the above general procedure: [1]H NMR (THF-d_8): 0.14 equiv of THF coordinated.

Example 454

$[2\text{-}(OH)\text{-}3,5\text{-}(NO_2)_2C_6H_2]\text{-}CH{=}NR$ [R = 1,2,3,4-tetrahydro-1-naphthyl]

The general procedure for imine synthesis was followed using 3.07 g (14.5 mmol) of 3,5-dinitrosalicylaldehyde and 2.55 g (1.20 equiv) of 1,2,3,4-tetrahydro-1-naphthylamine. A yellow powder (4.31 g, 87.1%) was isolated: [1]H NMR ($CDCl_3$) δ 8.98 (d, 1, Ar′: H), 8.36 (d, 1, Ar′: H), 8.07 (d, 1, Ar: H), 7.36 (m, 1, Ar: H), 7.27 (m, 3, N=C*H* and Ar: H), 7.15 (d, 1, Ar: H), 5.04 (m, 1, $NC\mathit{H}CH_2CH_2CH_2$), 2.90 (m, 2, $NCHCH_2CH_2C\mathit{H_2}$), 2.26, 1.97 and 1.87 (m′s, 2, 1 and 1 each, $NCHC\mathit{H_2}C\mathit{H_2}CH_2$).

The sodium salt was synthesized according to the above general procedure: [1]H NMR (THF-d_8): 0.11 equiv of THF coordinated.

Example 455

$[2\text{-}(OH)\text{-}3,5\text{-}I_2\text{-}C_6H_2]\text{-}CH{=}NAr$ [Ar = 2,6-(*i*-Pr)$_2$-C_6H_3]

The general procedure for imine synthesis was followed using 6.00 g (16.0 mmol) of 3,5-

diiodosalicylaldehyde and 3.70 g (1.31 equiv) of 2,6-diisopropylaniline. A yellow powder (7.93 g, 93.0%) was isolated: ^{1}H NMR ($CDCl_3$) δ 8.14 (d, 1, Ar′: H), 8.10 (s, 1, N=C*H*), 7.60 (d, 1, Ar′: H), 7.20 (m, 3, Ar: H), 2.92 (septet, 2, C*H*Me_2), 1.18 (d, 12, CH*Me_2*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.67 equiv of THF coordinated.

Example 456

$[2-(OH)-4,6-(OMe)_2-C_6H_2]-CH=NAr\ [Ar = 2,6-(i\text{-}Pr)_2-C_6H_3]$

The general procedure for imine synthesis was followed using 5.05 g (27.7 mmol) of 4,6-dimethoxysalicylaldehyde and 5.90 g (1.20 equiv) of 2,6-diisopropylaniline. A yellow powder (3.59 g, 38.0%) was isolated: ^{1}H NMR ($CDCl_3$) δ 8.58 (s, 1, N=C*H*), 7.18 (s, 3, Ar: H), 6.13 (d, 1, Ar′: H), 5.92 (d, 1, Ar′: H), 3.84 (s, 3, O*Me*), 3.80 (s, 3, O*Me′*), 3.03 (septet, 1, C*H*Me_2), 1.19 (d, 12, CH*Me_2*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): No THF coordinated.

Example 457

$[2\text{-Hydroxynaphthyl}]-CH=NAr\ [Ar = 2,6-Br_2-4-F-C_6H_2]$

The general procedure for imine synthesis was followed using 29.8 g (173 mmol) of 2-hydroxy-1-naphthaldehyde and 52.0 g (193 mmol) of 2,6-dibromo-4-fluoroaniline. A yellow powder (62.1 g, 84.9%, 2 crops) was isolated: ^{1}H NMR ($CDCl_3$) δ 9.40 (s, 1, N=C*H*), 8.09 (d, 1, Ar′: H), 7.92 (d, 1, Ar′: H), 7.81 (d, 1, Ar′: H), 7.55 (t, 1, Ar′: H), 7.43 (d, 2, Ar: H), 7.40 (t, 1, Ar′: H), 7.25 (d, 1, Ar′: H).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.66 equiv of THF coordinated.

Example 458

$[2\text{-Hydroxynaphthyl}]-CH=NAr\ [Ar = 2\text{-Aza-}6\text{-Me-}C_5H_3]$

The general procedure for imine synthesis was followed using 3.44 g (20.0 mmol) of 2-hydroxy-1-

naphthaldehyde and 2.59 g (1.20 equiv) of 2-amino-3-picoline. A yellow-orange powder (4.51 g, 86.0%) was isolated: ^{1}H NMR ($CDCl_3$) δ 9.94 (d,1, H_{aryl}), 8.27 (d, 1, N=C*H*), 8.09 (d, 1, H_{aryl}), 7.68 (d, 1, H_{aryl}), 7.54 (d, 1, H_{aryl}), 7.51 (d, 1, H_{aryl}), 7.44 (t, 1, H_{aryl}), 7.24 (t, 1, H_{aryl}), 7.02 (t, 1, H_{aryl}), 6.85 (d, 1, H_{aryl}), 2.44 (s, 3, *Me*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.1 equiv of THF coordinated.

Example 459

[2-Hydroxynaphthyl]-CH=NAr [Ar = 2-(*t*-Bu)-C_6H_4]

The general procedure for imine synthesis was followed using 10.19 g (59.2 mmol) of 2-hydroxy-1-naphthaldehyde and 10.60 g (1.20 equiv) of 2-*t*-butylaniline. A yellow powder (10.8 g, 60.4%) was isolated: ^{1}H NMR ($CDCl_3$) δ 9.27 (d, 1, N=C*H*), 8.18 (d, 1, H_{aryl}), 7.88 (d, 1, H_{aryl}), 7.79 (d, 1, H_{aryl}), 7.55 (t, 1, H_{aryl}), 7.52 (d, 1, H_{aryl}), 7.39 (t, 1, H_{aryl}), 7.37 (t, 1, H_{aryl}), 7.30 (t, 1, H_{aryl}), 7.21 (d, 1, H_{aryl}), 7.19 (d, 1, H_{aryl}), 1.52 (s, 9, C*Me*$_3$).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.48 equiv of THF coordinated.

Example 460

(Ar)(H)N-C(Me)=CH-C(O)-Ph [Ar = 2,6-(*i*-Pr)$_2$-C_6H_3]

The general procedure for imine synthesis was followed using 5.17 g (31.9 mmol) of 1-benzoylacetone and 7.35 g (1.30 equiv) of 2,6-diisopropylaniline. After 2 days, no precipitate formed from the methanol solution. However, slow evaporation of the methanol yielded single crystals, which were isolated and washed with a small amount of additional methanol. The standard work-up procedure was then followed to yield a white powder (2.56 g, 25.0%): ^{1}H NMR ($CDCl_3$) δ 7.89 (d, 2, H_{aryl}), 7.38 (m, 3, H_{aryl}), 7.25 (t, 1, H_{aryl}), 7.12 (d, 1, H_{aryl}), 5.86 (s, 1, =C*H*), 3.02 (septet, 2, C*H*Me$_2$), 1.71 (s, 3, N-C(*Me*)), 1.17 and 1.11 (d, 6 each,

CH*MeMe'*); ^{13}C NMR ($CDCl_3$) δ 188.4 (*C*(O)), 165.0 (N-*C*(Me)), 146.2 (Ar: C_o), 140.0 and 133.5 (Ph: C_{ipso}; Ar: C_{ipso}), 130.8 and 128.3 (Ar: C_p; Ph: C_p), 128.1, 127.1 and 123.5 (Ph: C_o, C_m; Ar: C_m), 92.1 (C(Me)=C*H*), 28.5 (*C*HMe$_2$), 24.6 and 22.7 (CH*MeMe'*), 19.7 (N-C(*Me*)).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.66 equiv of THF coordinated.

Example 461

[2-(OH)-C$_6$H$_4$-C=N-CMe$_2$-CH$_2$-O]

A 200 mL sidearm flask was charged with 5.0 g (42 mmol, 1.0 equiv) of 2-hydroxybenzonitrile, 5.6 g (63 mmol, 1.5 equiv) of 2-amino-2-methylpropanol, 0.29 g (2.1 mmol, 0.05 equiv) of $ZnCl_2$, and 90 mL of chlorobenzene. The reaction mixture was heated to reflux under N_2 atmosphere for 24 h. After this time, reflux was discontinued, the flask was cooled to ambient temperature, and most of the volatile materials were removed using a rotary evaporator. The resulting residue was dissolved in ~100 mL of CH_2Cl_2, transferred to a separatory funnel, and washed with 3 x 50 mL of H_2O. The combined H_2O washings were back extracted with ~30 mL of CH_2Cl_2, and the combined CH_2Cl_2 extracts were then dried over Na_2SO_4, filtered and evaporated to yield a brown oil which was purified by flash chromatography (SiO_2, eluting with 5:1 hexanes:EtOAc), to yield 6.3 g (78%) of the desired product: ^{1}H NMR ($CDCl_3$) δ 12.2 (br s, 1, O*H*), 7.6 (m, 1, H_{aryl}), 7.4 (m, 1, H_{aryl}), 7.06 (m, 1, H_{aryl}), 6.92 (m, 1, H_{aryl}), 4.14 (s, 2, C*H$_2$*), 1.44 (s, 6, C*Me$_2$*).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.20 equiv of THF coordinated.

Example 462

(4-Me-C$_6$H$_4$-N=P(Ph)$_2$-CH$_2$-(Ph)$_2$P=N-C$_6$H$_4$-4-Me)

See *Phosphorus, Sulfur, and Silicon* **1990**, *47*, 401. A 100-mL 3-neck round-bottomed flask was fitted with a condenser, a nitrogen inlet and an addition funnel. It

was charged with 2.64 g (6.87 mmol) of bis(diphenylphosphino)methane (DPPM) dissolved in 17 mL of benzene. The addition funnel was charged with 1.86 g (14.0 mmol) of 4-Me-C_6H_4-N_3 (prepared from *p*-toluidine hydrochloride, sodium nitrite and sodium azide, see Ugi, I; Perlinger, H.; Behringer, L. *Chemische Berichte* **1958**, *91*, 2330) dissolved in ca. 7-10 mL of benzene. The DPPM solution was heated to 60°C and the aryl azide solution slowly added to the reaction mixture. As the addition occurred, nitrogen was evolved. After the addition was completed, the reaction mixture was kept an additional 4 h at 60 °C. The solvent was then removed in vacuo, and the solid was collected, washed with 2 x 15mL of hexane and dried *in vacuo*. The yield was 3.75 g (92%): ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 8, PPh_2: H_o), 7.41 (t, 4, PPh_2: H_p), 7.29 (t, 3, PPh_2: H_m), 6.83 (d, 4, NAr: H_m), 6.52 (d, 4, NAr: H_o), 3.68 (t, 2, J_{HP} = 14.2, PCH_2P), 2.21 (s, 6, NAr: Me).

The sodium salt was synthesized according to the above general procedure: ^{1}H NMR (THF-d_8): 0.39 equiv of THF coordinated.

Example 463

(2-Me-C_6H_4-N=P(Ph)$_2$-CH_2-(Ph)$_2$P=N-C_6H_4-2-Me)

A 100-mL 3-neck round-bottomed flask was fitted with a condenser, a nitrogen inlet and an addition funnel. It was charged with 3.0 g (7.80 mmol) of bis(diphenylphosphino)methane (DPPM) dissolved in 20 mL of toluene. The addition funnel was charged with 2.11 g (15.8 mmol) of 2-Me-C_6H_4-N_3 (prepared from *o*-toluidine hydrochloride, sodium nitrite and sodium azide) dissolved in ca. 12 mL of toluene. The DPPM solution was heated to 60°C and the aryl azide solution slowly added to the reaction mixture. As the addition occurred, nitrogen was evolved. After the addition was completed, the reaction mixture was kept an additional 4 h at 60°C. The solvent was then removed *in vacuo*, the solid was collected and recrystallized from Et_2O/hexane. The yield was 2.70 g (58%). ^{1}H NMR

($CDCl_3$) δ 7.68 (m, 8, PPh_2: H_o), 7.38 (t, 4, PPh_2: H_p), 7.25 (t, 8, PPh_2: H_m), 7.09 (d, 2, NAr: H_m'), 6.76 (t, 2, NAr: H_m), 6.23 (t, 2, NAr: H_p), 6.23 (d, 2, NAr: H_o), 3.87 (t, 2, J_{HP} = 13.5, PCH_2P), 2.29 (s, 6, NAr: *Me*).

The sodium salt was synthesized according to the above general procedure: ^1H NMR (THF-d_8): 0.59 equiv of THF coordinated.

Example 464

Lithium 5-Methyl-2-Thiophenecarboxylate

The sodium salt was synthesized from commercially available 5-methyl-2-thiophenecarboxylic acid according to the above general procedure and the cation was exchanged with an excess of lithium chloride to improve product solubility: ^1H NMR (THF-d_8): 0.25 equiv of THF coordinated.

Example 465

$Cy_2PCH_2CH(CH_3)SLi$

A 100-mL Schlenk flask was charged with 1.28 g (6.28 mmol) of PCy_2Li (prepared from PCy_2H and n-BuLi) dissolved in 20 mL of THF. The flask was cooled to -78°C and propylene sulfide (520 mg, 7.01 mmol) was vacuum transferred onto the lithium salt solution. The reaction mixture was kept at -78°C for 45 min. The dry ice/acetone bath was then removed and the yellowish solution was allowed to warm to ambient temperature. After an additional 20 min, the solvent was removed in vacuo. The solid was washed three times with 30 mL of hexane and dried in vacuo. The yield was 1.37 g (78%). ^1H NMR (THF-d_8, 300 MHz, 23°C) δ 2.80 (m, 1, C*H*), 1.31 (d, 3, J= 6 Hz,, CH_3), 1-2 (m, 24, Cy_2, PCH_2); ^{31}P NMR: δ -7.6.

Example 466

Sodium 2,3,5,6-Tetrachloro-4-Pyridinethiolate

The sodium salt was synthesized according to the above general procedure from the commercially available 2,3,5,6-tetrachloro-4-pyridinethiol.

Example 467

Sodium 2,5-Dimethylpyrrole

The sodium salt was synthesized according to the above general procedure from the commercially available 2,5-dimethylpyrrole: ^{1}H NMR (THF-d_8): No THF coordinated.

Example 468

Sodium 2,6-Dibromo-4-Methylanilide

The sodium salt was synthesized according to the above general procedure from the commercially available 2,6-dibromo-4-methylaniline: ^{1}H NMR (THF-d_8): 0.5 equiv THF coordinated.

Examples 469-498

Complexes **21** through **49** were synthesized according to the general procedure for the synthesis of allyl initiators (see above under Examples 17-40).

Example 469

Complex **21a**. Two equiv (2.77 g, 6.45 mmol) of the sodium salt of the ligand were reacted with one equiv (1.53 g, 3.22 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 2.94 g (87.4% yield) of a yellow powder: ^{1}H NMR (C_6D_6) δ 7.39 (d, 1, Ar': H), 7.29 (d, 1, Ar': H), 7.0 - 6.9 (m, 3, Ar: H), 4.00 (m, 1, *H*H'CC(CO_2Me)C'HH'), 3.57 and 2.86 (septet, 1 each, C*H*Me_2 and C'*H*Me_2), 3.25 (s, 3, O*Me*), 2.86 (s, 1, HH'CC(CO_2Me)C'*H*H'), 1.92 (m, 1, H*H'*CC(CO_2Me)C'HH'), 1.47 (s, 3, N=C*Me*), 1.34, 1.18, 0.89 and 0.79 (d, 3 each, CH*MeMe'* and C'H*MeMe'*), 1.12 (s, 1 each, HH'CC(CO_2Me)C'H*H'*).

Example 470

Complex **21b**. Two equiv (720 mg, 1.68 mmol) of the sodium salt of the ligand were reacted with one equiv (225 mg, 0.834 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = H_2CCHCH_2) to give 599 mg (77.6% yield) of a yellow powder: ^{1}H NMR ($CDCl_3$) δ 7.39 (d, 1, Ar': H), 7.35 (d, 1, Ar': H), 7.13 - 7.00 (m, 3, Ar: H), 5.78 (m, 1, H_2CC*H*C'H_2), 3.66 and 3.07 (m, 1 each, C*H*Me_2 and C'*H*Me_2), 3.21, 2.64, 1.44 and 1.11 (d, 1 each, *HH'*CCHC'*HH'*),

1.99 (s, 3, N=C*Me*), 1.31, 1.26, 1.07 and 0.99 (d, 3 each, CH*MeMe'* and C'H*MeMe'*); ^{13}C NMR ($CDCl_3$) δ 168.7 (N=*C*Me), 159.5, 150.0, 137.7, 137.0, 131.8, 128.7, 127.9, 125.9, 123.8, 123.3, 120.9, 117.1, 113.1 (Ar: C_o, C_o', C_m, C_m', C_p, Ar': C_o, C_o', C_m, C_m', C_p, H_2CCHCH_2), 59.4 and 52.8 ($H_2CCHC'H_2$), 28.3 and 27.8 (*C*HMe$_2$, *C'*HMe$_2$), 24.1, 23.64, 23.54 and 23.4 (CH*MeMe'* and C'H*MeMe'*), 20.3 (N=C*Me*).

Example 471

Complex **22a**. Two equiv (809 mg, 2.14 mmol) of the sodium salt of the ligand were reacted with one equiv (508 mg, 1.07 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 792 mg (79.6% yield) of a yellow powder: ^{1}H NMR (C_6D_6) δ 7.57 (d, 1, Ar': H), 7.30 (d, 1, Ar': H), 7.0 - 6.9 (m, 3, Ar: H), 4.10 (m, 1, *H*H'CC(CO_2Me)C'HH'), 3.38 (s, 3, O*Me*), 2.69 (s, 1, HH'CC(CO_2Me)C'*H*H'), 2.02 and 2.12 (s, 3, Ar: *Me, Me'*), 1.89 (m, 1, H*H'*CC(CO_2Me)C'HH'), 1.45 (s, 3, N=C*Me*), 1.35 (s, 1, HH'CC(CO_2Me)C'H*H'*).

Example 472

Complex **23a**. Two equiv (1.56 g, 4.20 mmol) of the sodium salt of the ligand were reacted with one equiv (1.00 g, 2.10 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 1.35 g (65.3% yield) of a yellow powder: According to the ^{1}H NMR spectrum, two isomers (*t*-Bu group positioned syn and anti to the CO_2Me group) are present in a 1:1 ratio. ^{1}H NMR (C_6D_6) δ 7.6 - 6.5 (m, 8, H_{aryl}), 4.16 and 4.01 (s, 1 each, *H*H'CC(CO_2Me)C'HH' of each isomer), 3.42 and 3.42 (s, 3 each, O*Me* of each isomer), 2.82 and 2.74 (s, 1 each, HH'CC(CO_2Me)C'*H*H' of each isomer), 2.22 and 2.02 (s, 1 each, H*H'*CC(CO_2Me)C'HH' of each isomer), 1.63 and 1.56 (s, 3 each, N=C*Me* of each isomer), 1.56 and 1.38 (s, 9 each, C*Me$_3$* of each isomer), 1.54 and 1.36 (s, 1 each, HH'CC(CO_2Me)C'H*H'* of each isomer).

Example 473

Complex **24a**. Two equiv (1.10 g, 2.15 mmol) of the sodium salt of the ligand were reacted with one equiv

(512 mg, 1.08 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 635 mg (49.5% yield) of a yellow powder: ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 1, N=C*H*), 7.70 (d, 1, Ar': H), 7.20 - 7.08 (m, 4, Ar: H, Ar': H), 3.90 (d, 1, *H*H'CC(CO_2Me)C'HH'), 3.80 (s, 3, O*Me*), 3.73 and 2.92 (septet, 1 each, C*H*Me_2 and C'*H*Me_2), 2.99 (s, 1, HH'CC(CO_2Me)C'*H*H'), 2.03 (m, 1, H*H'*CC(CO_2Me)C'HH'), 1.56 (s, 1, HH'CC(CO_2Me)C'H*H'*), 1.30, 1.22, 1.08 and 0.93 (d, 3 each, CH*MeMe'* and C'H*MeMe'*).

Example 474

Complex **25a**. Two equiv (3.25 g, 6.31 mmol) of the sodium salt of the ligand were reacted with one equiv (1.50 g, 3.16 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 3.49 g (90.6% yield) of a yellow powder: ^{1}H NMR spectrum is clean and consistent with the desired product.

Example 475

Complex **26a**. Two equiv (2.01 g, 4.20 mmol) of the sodium salt of the ligand were reacted with one equiv (1.00 g, 2.10 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 1.51 g (64.9% yield) of a golden brown powder: ^{1}H NMR (C_6D_6) δ 7.64 (s, 1, Ar': H), 7.25 (s, 1, Ar': H), 6.70 (, 3, Ar: H), 3.85 (s, 1, *H*H'CC(CO_2Me)C'HH'), 3.15 (s, 3, O*Me*), 2.44 (s, 1, HH'CC(CO_2Me)C*H*H'), 1.97 and 1.85 (s, 3 each, Ar: *Me*, *Me'*), 1.60 (s, 1, H*H'*CC(CO_2Me)C'HH'), 1.20 (s, 3, N=C*Me*), 1.11 (s, 1, HH'CC(CO_2Me)C'H*H'*); ^{13}C NMR (C_6D_6, selected resonances) δ 59.5, 52.7, and 51.3 (H_2*C*C(CO_2*Me*)*C'*H_2), 19.0, 18.6, and 18.0 (N=C*Me*, Ar: *Me*, *Me'*).

Example 476

Complex **27a**. Two equiv (951 mg, 2.13 mmol) of the sodium salt of the ligand were reacted with one equiv (505 mg, 1.06 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 851 mg (68.6% yield) of a yellow powder: ^{1}H NMR spectrum in C_6D_6 is clean and consistent with the desired product. The product exists as a 1:1

ratio of isomers (t-Bu group positioned syn or anti to the CO_2Me group.)

Example 477

Complex **28a**. Two equiv (983 mg, 2.14 mmol) of the sodium salt of the ligand were reacted with one equiv (509 mg, 1.07 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 1.02 g (90.9% yield) of a green powder: ^1H NMR spectrum in C_6D_6 is broad, but consistent with the desired product. The product exists as an ~1:1 ratio of isomers (t-Bu group positioned syn or anti to the CO_2Me group.)

Example 478

Complex **29a**. Two equiv (550 mg, 1.59 mmol) of the sodium salt of the ligand were reacted with one equiv (308 mg, 0.647 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 478 mg (64.3% yield) of a dark brown powder.

Example 479

Complex **30a**. Two equiv (478 mg, 1.27 mmol) of the sodium salt of the ligand were reacted with one equiv (303 mg, 0.637 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 375 mg (61.4% yield) of a dark brown powder:

Example 480

Complex **31a**. Two equiv (1.04 g, 2.10 mmol) of the sodium salt of the ligand were reacted with one equiv (500 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 948 mg (81.1% yield) of a green-yellow powder: ^1H NMR (THF-d_8) δ 7.85, 7.34, 7.14, 7.12, 6.63 and 6.43 (N=CH, H_{aryl}, CHPh$_2$), 3.72 (s, 3, OMe), 3.80, 2.78, 2.78, and 1.48 (s, 1 each, HH'CC(CO_2Me)C'HH'), 1.37 and 1.18 (CMe_3, C'Me_3); ^{13}C NMR (THF-d_8) δ 166.9 (N=CH), 167.1, 166.9, 164.1, 142.3, 142.0, 140.9, 135.8, 130.3, 130.0, 129.4, 129.3, 129.27, 128.3, 118.3, 110.4 (C_{aryl} and $H_2C\mathit{C}(\mathit{C}O_2Me)CH_2$), 81.0 ($\mathit{C}HPh_2$), 59.1 and 45.8 ($H_2$CC($CO_2Me$)$\mathit{C}H_2$), 52.6 (O$Me$), 35.9 and 34.3 ($\mathit{C}Me_3$, C'Me$_3$), 31.7 and 29.7 (CMe_3, C'Me_3).

Example 481

Complex **32a**. Two equiv (923 mg, 2.15 mmol) of the sodium salt of the ligand were reacted with one equiv (512 mg, 1.08 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 907 mg (81.1% yield) of a brown-orange powder.

Example 482

Complex **33a**. Two equiv (891 mg, 2.11 mmol) of the sodium salt of the ligand were reacted with one equiv (502 mg, 1.06 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 940 mg (89.1% yield) of a gold powder. Two major isomers are present in a 1.18:1 ratio. There is a very small amount of a third product or isomer present. The ^1H NMR assignments of the two major isomers follow: ^1H NMR ($CDCl_3$) δ 8.30 and 8.25 (d, 1 each, Ar′: H of each isomer), 7.48 and 7.32 (d, 1 each, Ar′: H of each isomer), 6.94 and 6.78 (s, 1 each, N=C*H* of each isomer), 7.05 (m, 2, H_{aryl}), 6.83 (m, 1, H_{aryl}), 6.80 (m, 3, H_{aryl}), 6.58 (d, 1, H_{aryl}), 6.45 (m, 1, H_{aryl}), 3.90 and 3.73 (m, 1 each, *H*H′CC(CO_2Me)C′HH′ of each isomer), 3.18 and 3.09 (s, 3 each, O*Me* of each isomer), 2.43 and 2.41 (s, 1 each, HH′CC(CO_2Me)C′*H*H′ of each isomer), 2.26 and 2.08 (m, 1 each, H*H′*CC(CO_2Me)C′HH′ of each isomer), 1.30 and 1.17 (s, 1 each, HH′CC(CO_2Me)C′H*H′* of each isomer), 1.18 and 1.03 (s, 9 each, C*Me*$_3$ of each isomer).

Example 483

Complex **34a**. Two equiv (719 mg, 1.95 mmol) of the sodium salt of the ligand were reacted with one equiv (464 mg, 0.977 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 928 mg (96.6% yield) of a yellow powder. The ^1H NMR spectrum indicates that two isomers (Cl group positioned syn and anti to the CO_2Me group) are present in a 2.5 to 1 ratio. Major Isomer: ^1H NMR (C_6D_6) δ 8.50 (d, 1, Ar′: H), 7.52 (d, 1, Ar′: H), 7.10 (d, 1, Ar: H), 6.75 (t, 1, Ar: H), 6.72 (s, 1, N=C*H*), 6.70 (d, 1, Ar: H), 4.02 (d, 1, *H*H′CC(CO_2Me)C′HH′), 3.28 (s, 3, O*Me*), 2.60 (s, 1, HH′CC(CO_2Me)C′*H*H′), 2.18

(d, 1, H*H'*CC(CO_2Me)C'HH'), 1.99 (s, 3, Ar: *Me*), 1.63 (s, 1, HH'CC(CO_2Me)C'H*H'*); Minor Isomer: ^{1}H NMR (C_6D_6) δ 8.50 (d, 1, Ar': H), 7.53 (d, 1, Ar': H), 7.06 (d, 1, Ar: H), 6.8 - 6.7 (m, 3, N=C*H*, Ar: H), 4.10 (d, 1, *H*H'CC(CO_2Me)C'HH'), 3.39 (s, 3, O*Me*), 2.57 (s, 1, HH'CC(CO_2Me)C'*H*H'), 2.19 (d, 1, H*H'*CC(CO_2Me)C'HH'), 1.98 (s, 3, Ar: *Me*), 1.35 (s, 1, HH'CC(CO_2Me)C'H*H'*).

Example 484

Complex **35a**. Two equiv (765 mg, 2.11 mmol) of the sodium salt of the ligand were reacted with one equiv (500 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 890 mg (84.7% yield) of a red powder.

Example 485

Complex **36a**. Two equiv (1.22 g, 2.10 mmol) of the sodium salt of the ligand were reacted with one equiv (500 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 1.18 g (81.7% yield) of a yellow powder: ^{1}H NMR (CD_2Cl_2) δ 8.03 (d, 1, Ar': H), 7.70 (s, 1, N=C*H*), 7.36 (d, 1, Ar': H), 7.20 - 7.07 (m, 3, Ar: H), 3.88 (m, 1, *H*H'C(CO_2Me)C'HH'), 3.78 (s, 3, O*Me*), 3.71 (septet, 1, C*H*Me$_2$), 2.97 (s, 1, HH'CC(CO_2Me)C'*H*H'), 2.90 (septet, 1, C'*H*Me$_2$), 1.96 (m, 1, H*H'*CC(CO_2Me)C'HH'), 1.57 (s, 1 HH"CC(CO_2Me)CH*H'*), 1.28, 1.20, 1.04 and 0.90 (d, 3 each, CH*MeMe'*, C'H*MeMe'*); ^{13}C NMR (CD_2Cl_2) δ 166.8 (N=*C*H), 167.9, 164.6, 153.2, 151.6, 144.4, 141.4, 140.6, 128.4, 125.3, 125.2, 121.1, 114.2, 98.2 and 75.2 (Ar: C_o, C_o', C_m, C_m', C_p; Ar': C_o, C_o', C_m, C_m', C_p; H$_2$C*C*(*C*O$_2$Me)C'H$_2$), 62.7, 54.5 and 50.2 (H$_2$*C*C(CO$_2$*Me*)*C'*H$_2$), 30.2 and 29.8 (*C*HMe$_2$, *C'*HMe$_2$), 26.7, 26.5, 24.2 and 23.7 (CH*MeMe'*, C'H*MeMe'*).

Example 486

Complex **37a**. Two equiv (771 mg, 2.12 mmol) of the sodium salt of the ligand were reacted with one equiv (504 mg, 1.06 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 992 mg (93.9% yield) of a green powder: ^{1}H NMR (CD_2Cl_2) δ 8.25 (s, 1, N=C*H*), 7.18 (m,

3, Ar: H), 6.02 (d, 2, Ar': H), 5.68 (d, 2, Ar': H), 3.90 (septet, 1, C*H*Me_2), 3.84, 3.78 and 3.71 (s, 3 each, Ar: O*Me* and O*Me'*; CO_2*Me*), 3.65 (s, 1, *H*H'CC(CO_2Me)C'HH'), 3.03 (septet, 1, C'*H*Me_2), 2.80 (s, 1, HH'CC(CO_2Me)C'*H*H'), 1.88 (s, 1, H*H'*CC(CO_2Me)C'HH'), 1.46 (s, 1, HH'CC(CO_2Me)C'H*H'*), 1.36, 1.28, 1.14 and 0.99 (d, 3 each, CH*MeMe'*, C'H*MeMe'*).

Example 487

Complex **38a**. Two equiv (1.04 g, 2.12 mmol) of the sodium salt of the ligand were reacted with one equiv (503 mg, 1.06 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 1.10 g (89.3% yield) of a green-yellow powder: ^1H NMR (CD_2Cl_2) δ 8.65 (s, 1, N=C*H*), 7.84 (d, 1, Ar': H), 7.77 (d, 1, Ar': H), 7.68 (t, 1, Ar': H), 7.48 (m, 2, Ar: H), 7.44 (t, 1, Ar': H), 7.27 (t, 1, Ar': H), 7.07 (d, 1, Ar': H), 3.86 (s, 3, O*Me*), 3.80, 2.84, 2.05 and 1.91 (s, 1 each, *HH'*CC(CO_2Me)C'*HH'*).

Example 488

Complex **39a**. Two equiv (614 mg, 2.10 mmol) of the sodium salt of the ligand were reacted with one equiv (500 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 683 mg (77.6% yield) of a green-yellow powder: ^1H NMR (C_6D_6) δ 9.17 (s, 1, N=C*H*), 8.39 (d, 1, H_{aryl}), 7.62 (d, 1, H_{aryl}), 7.52 (d, 1, H_{aryl}), 7.52 (d, 1, H_{aryl}), 7.44 (d, 1, H_{aryl}), 7.24 (t, 1, H_{aryl}), 7.18 (t, 1, H_{aryl}), 7.11 (d, 1, H_{aryl}), 6.75 (dd, 1, H_{aryl}), 4.19 (br s, 1, *H*H'CC(CO_2Me)C'HH'), 3.43 (s, 3, O*Me*), 2.67 (br s, 1, HH'CC(CO_2Me)C'*H*H'), 2.32 (br s, 1, H*H'*CC(CO_2Me)C'HH'), 2.24 (s, 3, Ar: *Me*), 1.65 (s, 1, HH'CC(CO_2Me)C'H*H'*).

Example 489

Compound **40a**. Two equiv (765 mg, 2.12 mmol) of the sodium salt of the ligand were reacted with one equiv (505 mg, 1.06 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 925 mg (95.1% yield) of a green powder: Three isomers or products are present in a 1.35 to 1.02 to 1.00 ratio. ^1H NMR ($CDCl_3$,

selected resonances only) δ 8.84, 8.72 and 8.20 (N=C*H* of the 3 products), 3.29 (O*Me* of the 3 products--all overlapping), 1.81, 1.45 and 1.25 (CMe_3 of the 3 products).

Example 490

Complex **41a**. Two equiv (867 mg, 2.22 mmol) of the sodium salt of the ligand were reacted with one equiv (527 mg, 1.11 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 782 mg (77.1% yield) of a golden brown powder: ^{1}H NMR (C_6D_6) δ 8.08 (d, 2, Ph: C_o), 7.27 (m, 6, Ph: C_m, C_p; Ar: C_m, C_p), 6.01 (s, 1, PhCC*H*CMe), 4.23 (s, 1, *H*H'CC(CO_2Me)C'HH'), 4.03 (septet, 1, C*H*Me$_2$), 3.45 (s, 3, O*Me*), 3.33 (septet, 1, C'*H*Me$_2$), 3.04 (s, 1, HH'CC(CO_2Me)C'*H*H'), 2.18 (s, 1, H*H'*CC(CO_2Me)CHH'), 1.69 (s, 3, C*Me*NAr), 1.38 (s, 1, HH'CC(CO_2Me)CH*H'*), 1.54, 1.41, 1.29 and 1.18 (d, 3 each, CH*MeMe'* and C'H*MeMe'*).

Example 491

Complex **42a**. Two equiv (495 mg, 2.17 mmol) of the sodium salt of the ligand were reacted with one equiv (516 mg, 1.09 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 434 mg (57.4% yield) of a yellow powder: ^{1}H NMR (C_6D_6) δ 7.82 (d, 1, H_{aryl}), 7.20 (d, 1, H_{aryl}), 7.10 (t, 1, H_{aryl}), 6.47 (t, 1, H_{aryl}), 4.10 (s, 1, *H*H'CC(CO_2Me)C'HH'), 3.27 (s, 3, O*Me*), 3.27 (s, 2, OCH_2, overlaps with OMe), 3.02, 2.73 and 1.11 (s, 1 each, H*H'*CC(CO_2Me)C'*HH'*), 0.81 and 0.73 (s, 3 each, C*MeMe'*).

Example 492

Complex **43a**. Two equiv (586 mg, 0.909 mmol) of the sodium salt of the ligand were reacted with one equiv (216 mg, 0.455 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 506 mg (74.1% yield) of a dark red powder: ^{1}H NMR (THF-d_8) δ 7.50 (m, 8, PPh: H_o), 7.20 (t, 4, PPh: H_p), 7.10 (t, 8, PPh: H_m), 6.65 (d, 4, NAr: H_m), 6.59 (d, 4, NAr: H_o), 3.52 (s, 3, O*Me*), 2.77 (s, 2, *H*H'CC(CO_2Me)C*H*H'), 2.03 (s, 6, NAr: *Me*), 2.03 or 1.81 (m, 1, PC*H*P), 1.72 (s, 2, H*H'*CC(CO_2Me)CH*H'*); ^{13}C NMR (THF-d_8, selected resonances only) δ 50.9 and 47.9

($H_2CC(CO_2Me)CH_2$), 19.5 (NAr: *Me*), 12.0 (t, J_{CP} = 109 Hz, P*C*HP).

Example 493

Complex **44a**. Two equiv (343 mg, 0.520 mmol) of the sodium salt of the ligand were reacted with one equiv (124 mg, 0.260 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 128 mg (32.8% yield) of an orange powder. The ^{1}H NMR spectrum is consistent with the presence of one major symmetrical isomer; some of the ligand is also present along with some impurities and possibly the presence of other isomers. (The three possible isomers include the isomer with both methyl groups anti to the CO_2Me group, the isomer with both methyl groups syn to the CO_2Me group, and the isomer with one Me group anti and one Me group syn to the CO_2Me group). The nonaromatic resonances of the major symmetrical isomer follow: ^{1}H NMR (THF-d_8) δ 3.60 (s, 3, O*Me*), 2.77 (s, 2, *H*H'CC(CO_2Me)C*H*H'), 3.47 or 2.01 (m, 1, PC*H*P), 1.88 (s, 6, Ar: *Me*), 1.75 (s, 2, H*H'*CC(CO_2Me)CH*H'*).

Example 494

Complex **45a**. Two equiv (349 mg, 2.10 mmol) of the lithium salt of the ligand were reacted with one equiv (500 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 255 mg (40.7% yield) of an brown-yellow powder. ^{1}H NMR (C_6D_6/THF-d_8) δ 6.02 (s, 1, Thiophene: H), 5.23 (s, 1, Thiophene: H), 3.78 (br s, 1, *H*H'CC(CO_2Me)C'HH'), 3.40 and 3.38 (s, 3 each, Thiophene: *Me* and CO_2*Me*), 2.41 (s, 2, H*H'*CC(CO_2Me)C'*H*H'), 2.02 (s, 1, HH'CC(CO_2Me)CH*H'*).

Example 495

Complex **46a**. Two equiv (587 mg, 2.11 mmol) of the lithium salt of the ligand were reacted with one equiv (501 mg, 1.05 mmol) of [(allyl)Ni(μ-Br)]$_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 765 mg (84.5% yield) of an orange powder. ^{1}H NMR spectrum in C_6D_6 is complex. Peaks consistent with two different isomers of the product are present.

Example 496

Complex **47a**. Two equiv (607 mg, 2.24 mmol) of the sodium salt of the ligand were reacted with one equiv (303 mg, 1.12 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = H_2CCHCH_2) to give 482 mg (61.8% yield) of a red powder.

Example 497

Complex **48a**. Two equiv (149 mg, 1.27 mmol) of the sodium salt of the ligand were reacted with one equiv (302 mg, 0.635 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 146 mg (45.7% yield) of a red powder.

Example 498

Complex **49a**. Two equiv (700 mg, 2.17 mmol) of the sodium salt of the ligand were reacted with one equiv (515 mg, 1.08 mmol) of $[(allyl)Ni(\mu\text{-}Br)]_2$ (allyl = $H_2CC(CO_2Me)CH_2$) to give 779 mg (685.2% yield) of an orange powder. ^1H NMR spectrum in THF-d_8 is complex.

Examples 499-503

The following complexes of Examples through were synthesized by mixing the protonated form of the hydroxy-imine ligand with a base (e.g., pyridine, lutidine, acetonitrile, etc.) in an Et_2O solution and cooling this solution to -35 °C. The cold Et_2O solution was then added to a cold flask containing $(tmeda)NiMe_2$. [For the preparation of $(tmeda)NiMe_2$ please see: Kaschube, W.; Porschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525 - 532.] The reaction mixture was stirred for ~ 4 h. The solution was then filtered though a frit with dry Celite®. The solvent was removed and the product was dried in vacuo.

Example 499

Complex **50**. One equiv of $[2\text{-}(OH)\text{-}3,5\text{-}Cl_2\text{-}C_6H_2\text{-}C(Me){=}NAr$ [Ar = 2,6-$(i\text{-}Pr)_2$-C_6H_3] (356 mg, 0.976 mmol) was reacted with $(tmeda)NiMe_2$ (200 mg, 0.976 mmol) and pyridine (772 mg, 9.76 mmol) to yield an orange-red powder: ^1H NMR (C_6D_6) δ 8.66 (d, 2, Py: H_o), 7.50 (d, 1, Ar': H), 7.31 (d, 1, Ar': H), 7.09 (m, 3, Ar: H), 6.63 (t, 1, Py: H_p), 6.29 (t, 1, Py: H_m), 3.98 (septet,

2, C*H*Me_2), 1.68 (d, 6, CH*Me*Me′), 1.51 (s, 3, N=C*Me*), 1.04 (d, 6, CHMe*Me*′), -0.92 (s, 3, Ni*Me*).

Example 500

Complex **51**. One equiv of [2-(OH)-3,5-Cl_2-C_6H_2-C(Me)=NAr [Ar = 2,6-(*i*-Pr)$_2$-C_6H_3] (88.8 mg, 0.244 mmol) was reacted with (tmeda)$NiMe_2$ (50 mg, 0.244 mmol) and lutidine (26.2 mg, 0.244 mmol) to yield an orange powder: ^{1}H NMR (C_6D_6) δ 7.35 (d, 1, Ar′: H), 7.28 (d, 1, Ar′: H), 7.01 (s, 3, Ar: H), 6.64 (t, 1, Lutidine: H_p), 6.28 (d, 2, Lutidine: H_m), 3.91 (septet, 2, C*H*Me_2), 3.72 (s, 6, Lutidine: *Me*), 1.52 (d, 6, CH*Me*Me′), 1.46 (s, 3, N=C*Me*), 0.98 (d, 6, CHMe*Me*′), -1.42 (s, 3, Ni*Me*).

Example 501

Complex 52. One equiv of [2-(OH)-3,5-Cl_2-C_6H_2-C(Me)=NAr [Ar = 2,6-(*i*-Pr)$_2$-C_6H_3] (370 mg, 1.02 mmol) was reacted with (tmeda)$NiMe_2$ (209 mg, 1.02 mmol) and acetonitrile (10 mL) to yield a yellow-orange powder: ^{1}H NMR (CD_2Cl_2) δ 7.23 (d, 1, Ar′: H), 7.10 (t, 1, Ar: H_p), 7.04 (d, 2, Ar: H_m), 6.95 (d, 1, Ar′: H), 4.34 (septet, 2, C*H*Me_2), 1.89 (s, 3, N=C*Me*), 1.70 (s, 3, NC≡*Me*), 1.33 (d, 6, CH*Me*Me′), 1.15 (d, 6, CHMe*Me*′), 0.80 (s, 3, Ni*Me*).

Example 502

Complex **53**. One equiv of [2-(OH)-3,5-Cl_2-C_6H_2-C(Me)=NAr [Ar = 2,6-(*i*-Pr)$_2$-C_6H_3] (88.8 mg, 0.244 mmol) was reacted with (tmeda)$NiMe_2$ (50 mg, 0.244 mmol) and *p*-tolunitrile (28.6 mg, 0.244 mmol) to yield a brown powder: ^{1}H NMR (CD_2Cl_2) δ 7.74 (d, 2, Nitrile: H), 7.23 (d, 1, Ar′: H), 7.21 (d, 2, Nitrile: H), 7.10 (t, 1, Ar: H_p), 7.04 (d, 1, Ar: H_m), 6.95 (d, 1, Ar′: H), 4.34 (septet, 2, C*H*Me_2), 2.33 (s, 3, Nitrile: *Me*), 1.70 (s, 3, N=C*Me*), 1.33 (d, 6, CH*Me*Me′), 1.15 (d, 6, CHMe*Me*′), 0.80 (s, 3, Ni*Me*).

Example 503

Complex **54**. One equiv of [2-(OH)-3,5-Br_2-C_6H_2-C(Me)=NAr [Ar = 2,6-(*i*-Pr)$_2$-C_6H_3] (111 mg, 0.244 mmol) was reacted with (tmeda)$NiMe_2$ (50 mg, 0.244 mmol) and

pyridine (200 mg) to yield a yellow-orange powder: ^{1}H NMR (C_6D_6) δ 8.77 (d, 2, Py: H_o), 7.60 (t, 1, Py: H_p), 7.52 (d, 1, Ar': H), 7.44 (d, 1, Ar': H), 7.13 (t, 2, Py: H_m), 7.10 (s, 3, Ar: H), 3.85 (septet, 2, C*H*Me_2), 1.82 (s, 3, N=C*Me*), 1.51 (d, 6, CH*Me*Me'), 1.07 (d, 6, CHMe*Me'*), -1.42 (s, 3, Ni*Me*).

Examples 504-509

General Procedure for Ethylene(28-35 kPa)/α-Olefin Copolymerizations of Table 19

In the drybox, a glass Schlenk flask was loaded with the nickel compound, Lewis acid, solvent, comonomer, and a stir bar. The flask was then capped with a rubber septum and the stopcock was closed prior to removing the flask from the drybox. The flask was then attached to the ethylene line where it was evacuated and backfilled with ethylene. The reaction mixture was stirred under ethylene for the stated reaction time, the ethylene pressure was then released, and the polymer was precipitated by adding the reaction mixture to a solution of MeOH (~100 mL) and concentrated HCl (~1-3 mL). The solid polymer was then collected on a frit and rinsed with MeOH. For amorphous polymers, the MeOH was decanted off of the polymer. Often, the amorphous polymer was dissolved in hexane and reprecipitated in methanol. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. The polymer yield and characterization were then obtained.

For Example 505 the following quantitative ^{13}C NMR (TCB, 120-140°C) was obtained: Branching per 1000 CH_2's; total methyls (98.4), methyl (54.5), ethyl (13.1), propyl (3.2), butyl (14.4), amyl (4.9), hexyl and greater and end of chains (11.1), amyl and greater and end of chains (13.7), butyl and greater and end of chains (27.6)

For Example 506 the following quantitative ^{13}C NMR (TCB, 120-140°C) was obtained: Branching per 1000 CH_2's; total methyls (115.4), methyl (61.5), ethyl

(12.8), propyl (3.8), butyl (21.3), amyl (4.0), hexyl and greater and end of chains (14.4), amyl and greater and end of chains (16.3), butyl and greater and end of chains (37.2)

Table 19

Ethylene/α-Olefin Copolymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (h)	Toluene (mL)	Comonomer (mL)	Polymer (g)
504	3a	BPh_3/20	32	30	1-Hexene (10)	0.633
		Description: Viscous clear oil. ^1H NMR (C_6D_6, rt): 198.2 Total Me/1000 CH_2				
505	6a	$B(C_6F_5)_3$/20	24.2	30	1-Hexene (5)	7.31
		Description: Tough, rubbery, amorphous light tan solid. ^1H NMR (C_6D_6, rt): 116.1 Total Me/1000 CH_2				
506	6a	$B(C_6F_5)_3$/20	24.2	25	1-Hexene (10)	6.26
		Description: Rubbery, slightly sticky amorphous light tan solid. ^1H NMR (C_6D_6, rt): 129.9 Total Me/1000 CH_2				
507	6a	$B(C_6F_5)_3$/20	24.2	20	1-Hexene (15)	4.18
		Description: Sticky, very viscous oil--almost a solid. ^1H NMR (C_6D_6, rt): 167.9 Total Me/1000 CH_2				
508	6a	$B(C_6F_5)_3$/20	33.3	30	1-Octene (5)	5.65
		Description: Tough, amorphous rubbery solid. ^1H NMR (C_6D_6, rt): 112.0 Total Me/1000 CH_2				
509	9a	$B(C_6F_5)_3$/20	27.3	30	1-Octene (5)	7.53
		Description: Sticky, amorphous light tan solid. ^1H NMR (C_6D_6, rt): 178.7 Me/1000 CH_2				

Examples 510-512

General Procedure for Homopolymerizations of1-Hexene, 1-Octene, and Cyclopentene by Cmpd **6a** (Table 20)

In the drybox, the nickel compound, Lewis acid, solvent, monomer and stir bar were placed together in a round bottom flask. The reaction mixture was stirred for the stated amount of time. The flask was removed from the drybox and water and concentrated hydrochloric acid were added. The product was extracted with toluene and/or hexane and the solution was filtered through a frit containing a layer of neutral alumina on

top of a layer of silica gel. The solvent was then evaporated and the product was dried in vacuo.

Table 20

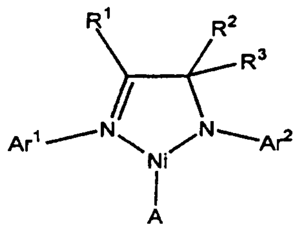
Ethylene/α-Olefin Copolymerizations at 28-35 kPa Ethylene

Ex.	Cmpd	Lewis Acid (equiv)	Time (weeks)	Toluene (mL)	Comonomer (mL)	Polymer (g)
510	6a	$B(C_6F_5)_3$/20	~2	5	1-Hexene (10)	0.511
		Description: Viscous oil. ^1H NMR (C_6D_6, rt): 152.2 Total Me per 1000 Carbon Atoms; DP ~ 17.4; M_n ~ 1,460				
511	6a	$B(C_6F_5)_3$/20	~2	5	1-Octene (10)	1.83
		Description: Free-flowing, slightly viscous oil. ^1H NMR (C_6D_6, rt): 122.8 Total Me per 1000 Carbon Atoms; DP ~ 10.5; M_n ~ 1,180				
512	6a	$B(C_6F_5)_3$/20	~2	5	Cyclopentene (10)	1.57
		Description: Partial viscous oil/partial solid. ^1H NMR (C_6D_6) indicates polycyclopentene formation with olefinic end groups present.				

CLAIMS

What is claimed is:

1. A process for the polymerization of an olefin selected from one or more of $R^{67}CH{=}CH_2$, cyclopentene, a styrene, a norbornene or $H_2C{=}CH(CH_2)_sCO_2R^{77}$, comprising, contacting, at a temperature of about $-100^{\circ}C$ to about $+200^{\circ}C$, $R^{67}CH{=}CH_2$, cyclopentene, a styrene, a norbornene, or $H_2C{=}CH(CH_2)_sCO_2R^{77}$, optionally a Lewis acid, and a compound of the formula: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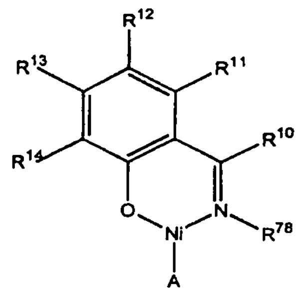
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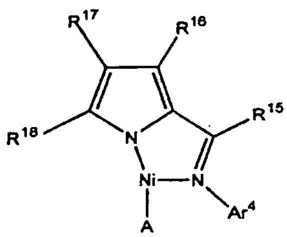
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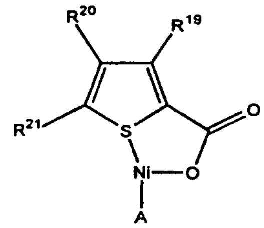
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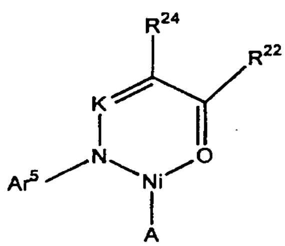
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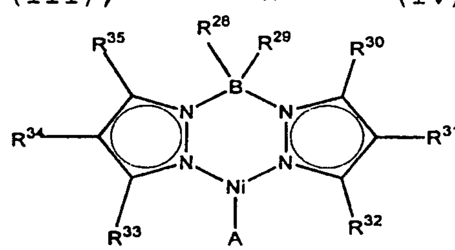
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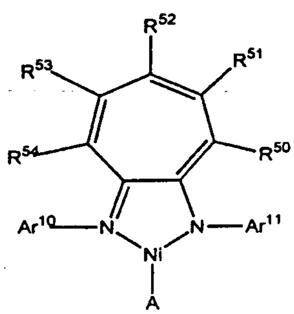
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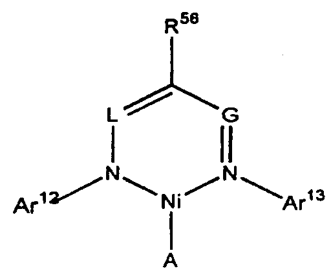
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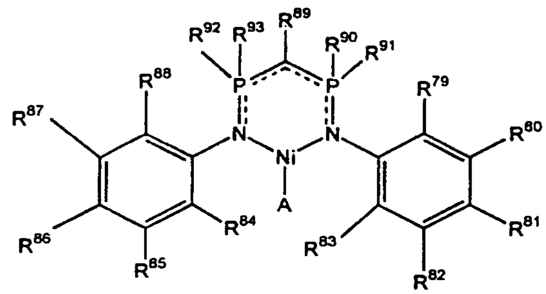

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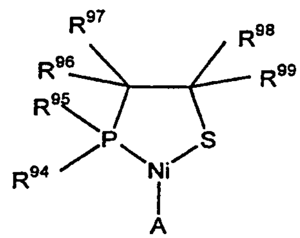

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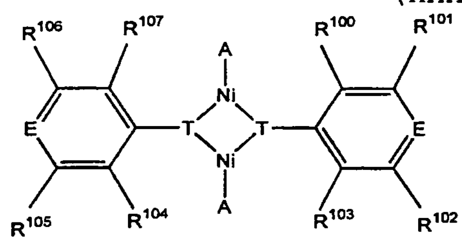

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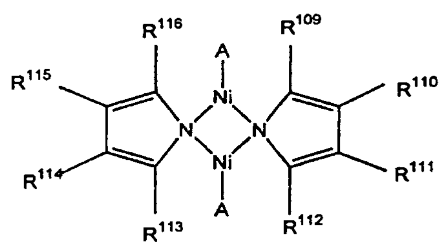


(XXXX)

wherein:

Ar^1, Ar^2, Ar^4, Ar^5, Ar^{10}, Ar^{11}, Ar^{12} and Ar^{13} are each independently aryl or substituted aryl;

R^1 and R^2 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^1 and R^2 taken together form a ring, and R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^1, R^2 and R^3 taken together form a ring;

A is a π-allyl or π-benzyl group;

R^{10} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{30}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35} R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

K is N or CR^{27};

R^{22} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{24} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{27} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{22} and R^{24} or R^{24} and R^{27} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

G and L are both N or G is CR^{57} and L is CR^{55};

R^{55}, R^{56} and R^{57} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or any two of R^{55}, R^{56} and R^{57} taken together form a ring;

R^{67} is hydrogen, alkyl or substituted alkyl;

R^{77} is hydrocarbyl or substituted hydrocarbyl;

R^{78} is hydrocarbyl or substituted hydrocarbyl;

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{94} and R^{95} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

both of T are S (sulfur) or NH (amino);

each E is N (nitrogen) or CR^{108} wherein R^{108} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

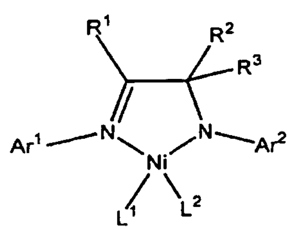
R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

s is an integer of 1 or more; and

R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that when $H_2C{=}CH(CH_2)_sCO_2R^{77}$ is present, $R^{67}CH{=}CH_2$ is also present.

2. A process for the polymerization of an olefin selected from one or more of $R^{67}CH{=}CH_2$, a styrene, a norbornene or $H_2C{=}CH(CH_2)_sCO_2R^{77}$, comprising, contacting, at a temperature of about -100°C to about +200°C, $R^{67}CH{=}CH_2$, cyclopentene, a styrene, a norbornene, or $H_2C{=}CH(CH_2)_sCO_2R^{77}$, optionally a Lewis acid, and a compound of the formula:



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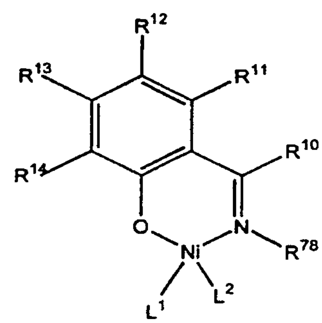

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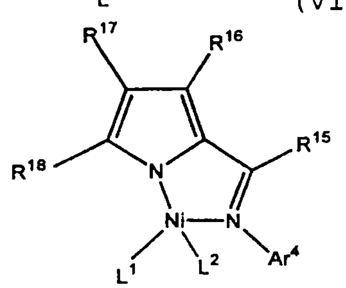

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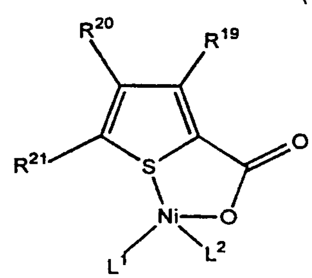

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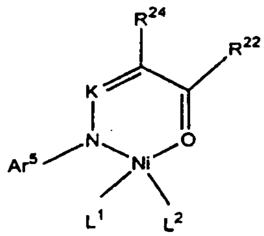

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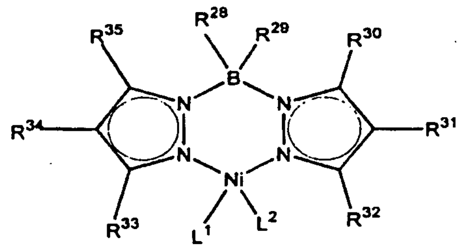
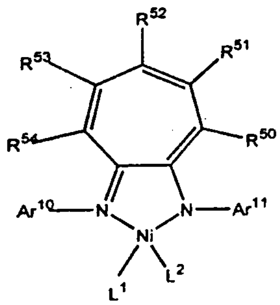
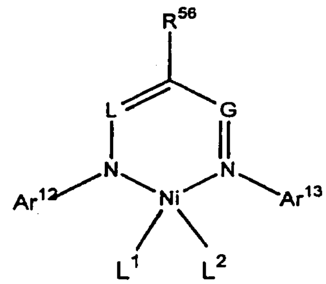


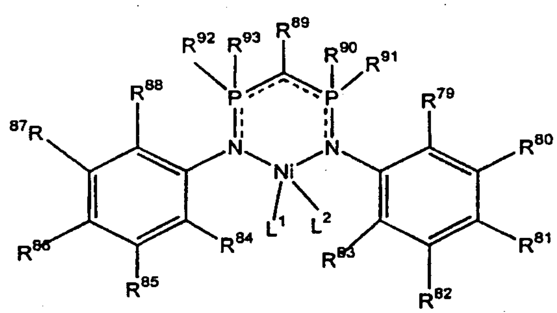
(XII),



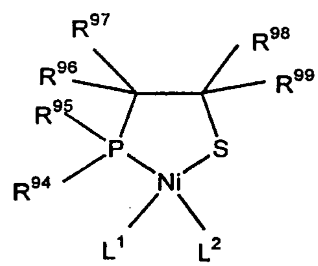
(XIX),



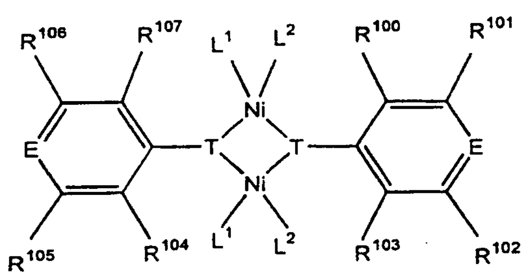
(XXVIII)



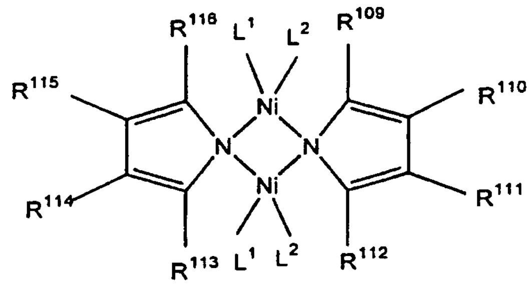
(XXXXI),



(XXXXII),



(XXXXIII), or



(XXXXIV),

wherein:

L^1 is a neutral monodentate ligand which may be displaced by said olefin, and L^2 is a monoanionic monodentate ligand, or L^1 and L^2 taken together are a monoanionic bidentate ligand, provided that said monoanionic monodentate ligand or said monoanionic bidentate ligand may add to said olefin;

Ar^1, Ar^2, Ar^4, Ar^5, Ar^{10}, Ar^{11}, Ar^{12} and Ar^{13} are each independently aryl or substituted aryl;

R^1 and R^2 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^1 and R^2 taken together form a ring, and R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^1, R^2 and R^3 taken together form a ring;

R^{10} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{30}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35}, R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

K is N or CR^{27};

R^{22} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{24} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{27} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{22} and R^{24} or R^{24} and R^{27} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

G and L are both N or G is CR^{57} and L is CR^{55};

R^{55}, R^{56} and R^{57} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or any two of R^{55}, R^{56} and R^{57} taken together form a ring;

R^{67} is hydrogen, alkyl or substituted alkyl;

R^{77} is hydrocarbyl or substituted hydrocarbyl;

R^{78} is hydrocarbyl or substituted hydrocarbyl;

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{94} and R^{95} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

both of T are S (sulfur) or NH (amino);

each E is N (nitrogen) or CR^{108} wherein R^{108} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

s is an integer of 1 or more; and

R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

and provided that when $H_2C{=}CH(CH_2)_sCO_2R^{77}$ is present, $R^{67}CH{=}CH_2$ is also present.

3. The process as recited in claim 1 or 2 wherein said temperature is about 0°C to about 150°C.

4. The process as recited in claim 1 or 2 wherein said temperature is about 25°C to about 100°C.

5. The process as recited in claim 1 or 2 wherein said Lewis acid is present.

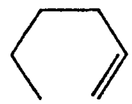
6. The process as recited in claim 1 or 2 wherein said Lewis acid is not present.

7. The process as recited in claim 1 or 2 wherein said compound is (I) or (VII).

8. The process as recited in claim 7 wherein:

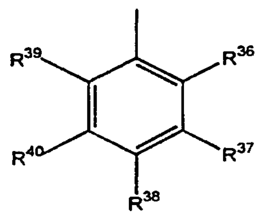
R^1 and R^2 are both hydrogen;

R^3 is alkyl or aryl containing 1 to 20 carbon atoms, or R^1, R^2 and R^3 taken together are



; and

Ar^1 and Ar^2 are each independently



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

9. The process as recited in claim 8 wherein R^3 is t-butyl, R^1 and R^2 are hydrogen, and R^{36} and R^{39} are halo, phenyl, or alkyl containing 1 to 6 carbon atoms.

10. The process as recited in claim 1 or 2 wherein said compound is (II) or (VIII).

11. The process as recited in claim 10 wherein:

R^{10} is hydrogen or methyl;

R^{78} is Ar^3, which is aryl or substituted aryl; and

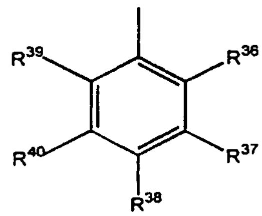
R^{11}, R^{12}, R^{13} and R^{14} are each independently chloro, bromo, iodo, alkyl, alkoxy, hydrogen or nitro, or R^{11} and R^{12} taken together form a 6-membered carbocyclic ring and R^{13} and R^{14} are hydrogen.

12. The process as recited in claim 1 or 2 wherein said compound is (III) or (IX).

13. The process as recited in claim 12 wherein:

R^{15}, R^{16}, R^{17} and R^{18} are hydrogen; and

Ar^{4} is



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

14. The process as recited in claim 1 or 2 wherein said compound is (IV) or (X).

15. The process as recited in claim 14 wherein R^{19}, R^{20} and R^{21} are hydrogen, or R^{19} and R^{20} are hydrogen and R^{21} is methyl.

16. The process as recited in claim 1 or 2 wherein said compound is (V) or (XI).

17. The process as recited in claim 16 wherein:

K is CR^{27};

R^{27} is hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{24} is hydrogen, alkyl or halo;

R^{22} is hydrocarbyl or $-OR^{117}$, wherein R^{117} is hydrocarbyl.

18. The process as recited in claim 17 wherein:

R^{27} is methyl;

R^{22} is phenyl, or $-OR^{117}$, R^{117} is alkyl containing 1 to 6 carbon atoms; and

R^{24} is hydrogen.

19. The process as recited in claim 1 or 2 wherein said compound is (VI) or (XII).

20. The process as recited in claim 19 wherein:

R^{32} and R^{33} are both alkyl containing 1 to 6 carbon atoms or phenyl, more preferably isopropyl, R^{28} and R^{29} are both hydrogen or phenyl, and R^{30}, R^{31}, R^{34} and R^{35} are all hydrogen; or

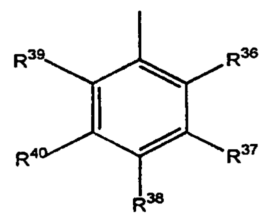
R^{31} and R^{32} taken together and R^{33} and R^{34} taken together are both a 6-membered aromatic carbocyclic ring having a t-butyl group vicinal to the R^{32} and R^{33} positions, and R^{28} and R^{29} are both hydrogen.

21. The process as recited in claim 1 or 2 wherein said compound is (XVIII) or (XIX).

22. The process as recited in claim 21 wherein:

R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are hydrogen; and

Ar^{10} and Ar^{11} are each independently



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

23. The process as recited in claim 1 or 2 wherein said compound is (XXVII) or (XXVIII).

24. The process as recited in claim 23 wherein:

L is CR^{55};

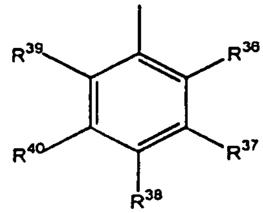
R^{55} is hydrocarbyl, hydrogen, or substituted hydrocarbyl;

G is CR^{57};

R^{57} is hydrocarbyl, hydrogen or substituted hydrocarbyl;

R^{56} is hydrogen; and

Ar^{12} and Ar^{13} are each independently



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

25. The process as recited in claim 24 wherein R^{55} and R^{57} are both alkyl or fluorinated alkyl, and Ar^{12} and Ar^{13} are both 2,6-diisopropylphenyl.

26. The process as described in claim 1 or 2 wherein said compound is (XXXVII) or (XXXXI).

27. The process as recited in claim 26 wherein:

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen or alkyl; and

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl.

28. The process as described in claim 1 or 2 wherein said compound is (XXXVIII) or (XXXXII).

29. The process as recited in claim 28 wherein:

R^{94} and R^{95} are each independently hydrocarbyl; and

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen or hydrocarbyl.

30. The process as recited in claim 1 or 2 wherein said compound is (XXXIX) or (XXXXIII).

31. The process as recited in claim 30 wherein:

E is N or CR^{108};

R^{108} is hydrogen or hydrocarbyl; and

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, or halo.

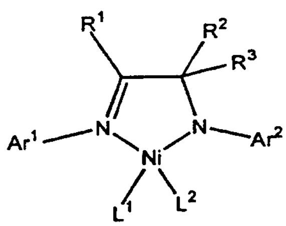
32. The process as recited in claim 1 or 2 wherein said compound is (XXXX) or (XXXXIV).

33. The process as recited in claim 32 wherein R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen or hydrocarbyl.

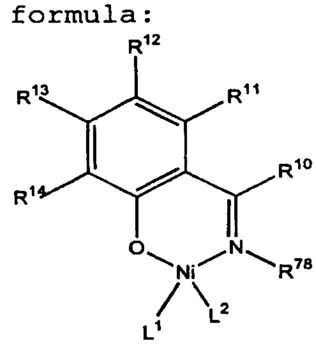
34. The process as recited in claim 2 wherein L^1 is a nitrile, pyridine or substituted pyridine, and L^2 is methyl.

35. The process as recited in claim 1 or claim 2 wherein said olefin or olefins are: ethylene; a styrene; a norbornene; an α-olefin; cyclopentene; $H_2C{=}CH(CH_2)_sCO_2R^{77}$ and ethylene; ethylene and an α-olefin; a styrene and a norbornene; and 2 or more norbornenes.

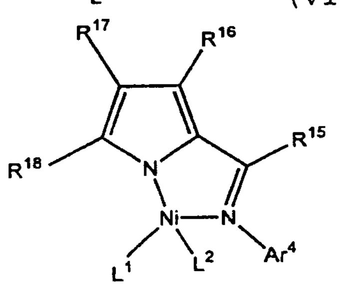
36. A compound of the formula:



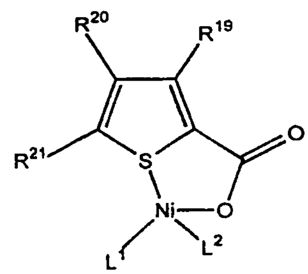
(VII),



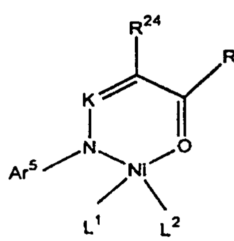
(VIII),



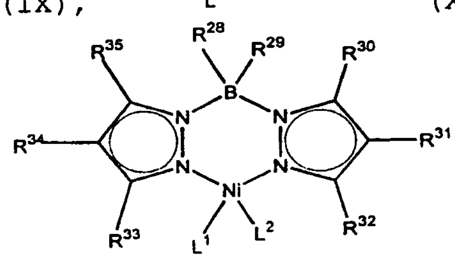
(IX),



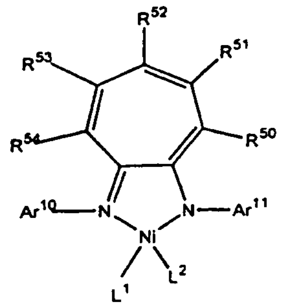
(X),



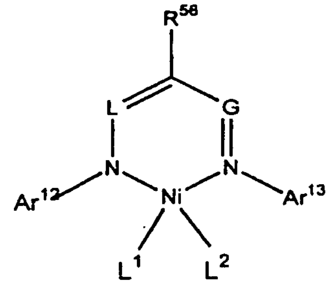
(XI), or



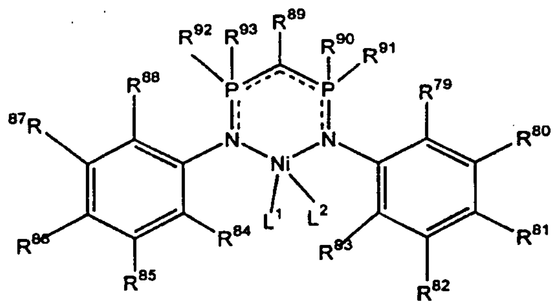
(XII),



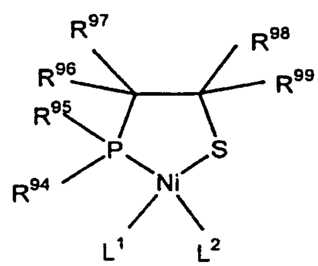
(XIX),



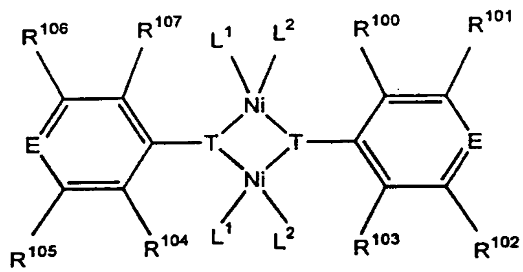
(XXVIII)



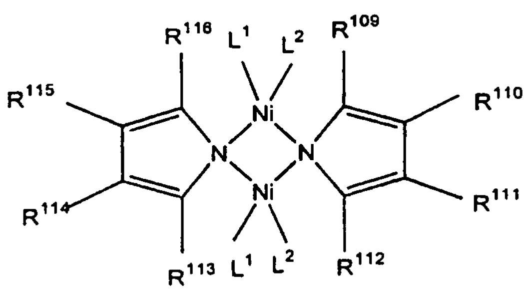
(XXXXI),



(XXXXII),



(XXXXIII), or



(XXXXIV),

wherein:

L^1 is a neutral monodentate ligand which may be displaced by said olefin, and L^2 is a monoanionic monodentate ligand, or L^1 and L^2 taken together are a monoanionic bidentate ligand, provided that said monoanionic monodentate ligand or said monoanionic bidentate ligand may add to said olefin;

Ar^1, Ar^2,Ar^4, Ar^5, Ar^{10}, Ar^{11}, Ar^{12} and Ar^{13} are each independently aryl or substituted aryl;

R^1 and R^2 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^1 and R^2 taken together form a ring, and R^3 is hydrogen, hydrocarbyl or substituted hydrocarbyl or R^1, R^2 and R^3 taken together form a ring;

R^{10} and R^{15} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{11}, R^{12}, R^{13}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{30}, R^{31}, R^{32}, R^{33}, R^{34}, R^{35}, R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, an inert functional group, and provided that any two of these groups vicinal to one another taken together may form a ring;

K is N or CR^{27};

R^{22} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{24} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{27} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{22} and R^{24} or R^{24} and R^{27} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

G and L are both N or G is CR^{57} and L is CR^{55};

R^{55}, R^{56} and R^{57} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl, or any two of R^{55}, R^{56} and R^{57} taken together form a ring;

R^{78} is hydrocarbyl or substituted hydrocarbyl;

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{94} and R^{95} are each independently hydrocarbyl or substituted hydrocarbyl;

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

both of T are S (sulfur) or NH (amino);

each E is N (nitrogen) or CR^{108} wherein R^{108} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group; and

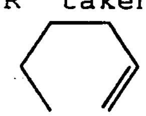
R^{28} and R^{29} are each independently hydrogen, hydrocarbyl or substituted hydrocarbyl.

37. The compound as recited in claim 36 which is (I) or (VII).

38. The compound as recited in claim 37 wherein:

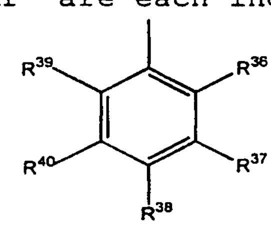
R^1 and R^2 are both hydrogen;

R^3 is alkyl or aryl containing 1 to 20 carbon atoms, or R^1, R^2 and R^3 taken together are



; and

Ar^1 and Ar^2 are each independently



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

39. The compound as recited in claim 38 wherein R^3 is t-butyl, R^1 and R^2 are hydrogen, and R^{36} and R^{39} are halo, phenyl, or alkyl containing 1 to 6 carbon atoms.

40. The compound as recited in claim 36 which is (II) or (VIII).

41. The compound as recited in claim 40 wherein:

R^{10} is hydrogen or methyl;

R^{78} is Ar^3, which is aryl or substituted aryl; and

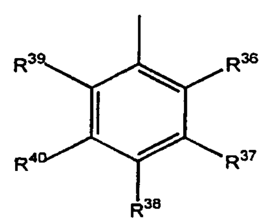
R^{11}, R^{12}, R^{13} and R^{14} are each independently chloro, bromo, iodo, alkyl, alkoxy, hydrogen or nitro, or R^{11} and R^{12} taken together form a 6-membered carbocyclic ring and R^{13} and R^{14} are hydrogen.

42. The compound as recited in claim 36 which is (III) or (IX).

43. The compound as recited in claim 42 wherein:

R^{15}, R^{16}, R^{17} and R^{18} are hydrogen; and

Ar^4 is



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

44. The compound as recited in claim 36 which is (IV) or (X).

45. The compound as recited in claim 44 wherein R^{19}, R^{20} and R^{21} are hydrogen, or R^{19} and R^{20} are hydrogen and R^{21} is methyl.

46. The compound as recited in claim 36 which is (V) or (XI).

47. The compound as recited in claim 46 wherein:

K is CR^{27};

R^{27} is hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group;

R^{24} is hydrogen, alkyl or halo;

R^{22} is hydrocarbyl or $-OR^{117}$, wherein R^{117} is hydrocarbyl.

48. The compound as recited in claim 47 wherein:

R^{27} is methyl;

R^{22} is phenyl, or $-OR^{117}$, R^{117} is alkyl containing 1 to 6 carbon atoms; and

R^{24} is hydrogen.

49. The compound as recited in claim 36 which is (VI) or (XII).

50. The compound as recited in claim 49 wherein:

R^{32} and R^{33} are both alkyl containing 1 to 6 carbon atoms or phenyl, more preferably isopropyl, R^{28} and R^{29} are both hydrogen or phenyl, and R^{30}, R^{31}, R^{34} and R^{35} are all hydrogen; or

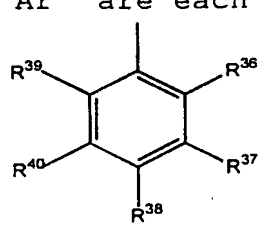
R^{31} and R^{32} taken together and R^{33} and R^{34} taken together are both a 6-membered aromatic carbocyclic ring having a t-butyl group vicinal to the R^{32} and R^{33} positions, and R^{28} and R^{29} are both hydrogen.

51. The compound as recited in claim 36 which is (XVIII) or (XIX).

52. The compound as recited in claim 51 wherein:

R^{50}, R^{51}, R^{52}, R^{53} and R^{54} are hydrogen; and

Ar^{10} and Ar^{11} are each independently



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted

hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

53. The compound as recited in claim 36 which is (XXVII) or (XXVIII).

54. The compound as recited in claim 53 wherein:

L is CR^{55};

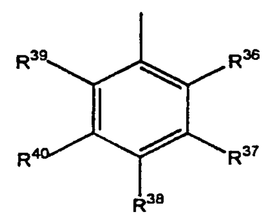
R^{55} is hydrocarbyl, hydrogen, or substituted hydrocarbyl;

G is CR^{57};

R^{57} is hydrocarbyl, hydrogen or substituted hydrocarbyl;

R^{56} is hydrogen; and

Ar^{12} and Ar^{13} are each independently



(XIV)

wherein R^{36}, R^{37}, R^{38}, R^{39} and R^{40} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group, provided that any 2 of R^{36}, R^{37}, R^{38}, R^{39} and R^{40} that are vicinal to one another taken together may form a ring.

55. The compound as recited in claim 54 wherein R^{55} and R^{57} are both alkyl or fluorinated alkyl, and Ar^{12} and Ar^{13} are both 2,6-diisopropylphenyl.

56. The compound as described in claim 36 which is (XXXVII) or (XXXXI).

57. The compound as recited in claim 56 wherein:

R^{79}, R^{80}, R^{81}, R^{82}, R^{83}, R^{84}, R^{85}, R^{86}, R^{87}, R^{88} and R^{89} are each independently hydrogen or alkyl; and

R^{90}, R^{91}, R^{92} and R^{93} are each independently hydrocarbyl.

58. The compound as described in claim 36 which is (XXXVIII) or (XXXXII).

59. The compound as recited in claim 58 wherein:

R^{94} and R^{95} are each independently hydrocarbyl; and

R^{96}, R^{97}, R^{98}, and R^{99} are each independently hydrogen or hydrocarbyl.

60. The compound as recited in claim 36 which is (XXXIX) or (XXXXIII).

61. The compound as recited in claim 60 wherein:

E is N or CR^{108};

R^{108} is hydrogen or hydrocarbyl; and

R^{100}, R^{101}, R^{102}, R^{103}, R^{104}, R^{105}, R^{106}, and R^{107} are each independently hydrogen, hydrocarbyl,or halo.

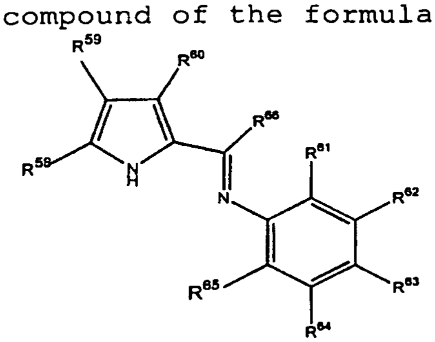
62. The compound as recited in claim 36 which is (XXXX) or (XXXXIV).

63. The compound as recited in claim 62 wherein R^{109}, R^{110}, R^{111}, R^{112}, R^{113}, R^{114}, R^{115} and R^{116} are each independently hydrogen or hydrocarbyl.

64. The compound as recited in claim 36 wherein L^1 is a nitrile, pyridine, or a substituted pyridine, and L^2 is methyl.

65. The compound as recited in claim 36 wherein L^1 and L^2 taken together are not π-allyl or π-benzyl.

66. A compound of the formula



(XXXIII),

wherein:

R^{58}, R^{59}, R^{60}, R^{62}, R^{63} and R^{64} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or a functional group, and provided that any two of these groups vicinal to one another taken together may form a ring, or if vicinal to R^{61} or R^{65} form a ring with them;

R^{66} is hydrogen, hydrocarbyl or substituted hydrocarbyl; and

R^{61} and R^{65} are each independently hydrocarbyl containing 2 or more carbon atoms, or substituted hydrocarbyl containing 2 or more carbon atoms, and provided that R^{61} and R^{65} may form a ring with any group vicinal to it.

67. The compound as recited in claim 66 wherein;

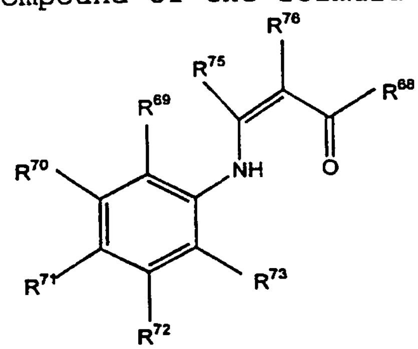
R^{58}, R^{59}, and R^{60} are hydrogen;

R^{66} is hydrogen;

R^{61} and R^{65} are each independently alkyl containing 2 or more carbon atoms; and

R^{62}, R^{63} and R^{64} are hydrogen.

68. A compound of the formula



(XXXVI),

wherein:

R^{68} is hydrocarbyl, substituted hydrocarbyl, $-SR^{117}$, $-OR^{117}$, or $-NR^{118}{}_2$, R^{76} is hydrogen, a functional group, hydrocarbyl or substituted hydrocarbyl, and R^{75} is hydrocarbyl or substituted hydrocarbyl, and provided that R^{68} and R^{76} or R^{75} and R^{76} taken together may form a ring;

R^{117} is hydrocarbyl or substituted hydrocarbyl;

each R^{118} is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R^{70}, R^{71} and R^{72} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

R^{69} and R^{73} are hydrocarbyl containing 3 or more carbon atoms, substituted hydrocarbyl containing 3 or more carbon atoms or a functional group;

and provided that any two of R^{70}, R^{71}, R^{72}, R^{69} and R^{73} vicinal to one another together may form a ring.

69. The compound as recited in claim 68 wherein:

R^{68} is $-OR^{117}$ or aryl;

R^{75} is hydrocarbyl or substituted hydrocarbyl; and

R^{76} is hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group.

70. The compound as recited in claim 69 wherein R^{76} is hydrogen, hydrocarbyl or substituted hydrocarbyl.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/00610

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/70 C08F4/82 C07F15/04 C07D207/335
C07C225/14 C07C229/30 C07C237/16 C07C327/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C07F C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 23010 A (DU PONT; UNIV NORTH CAROLINA (US)) 1 August 1996 see claims	1-65
A	DE 44 15 725 A (ECOLE EUROP DES HAUTES ETUDES) 10 November 1994 see claims	1-65
A	US 5 395 811 A (NOVAK BRUCE ET AL) 7 March 1995 see claims and figures 1A and 1B	1-65

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 May 1998	25/05/1998

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int   tional Application No
PCT/US 98/00610

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